

FINAL REPORT

Submitted To
THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

BY

Universities Space Research Association
The American City Building, Suite 212
Columbia, Maryland 21044

***PRELIMINARY DEFINITION PHASE
CRYSTAL GROWTH OF ZnSe AND RELATED TERNARY
COMPOUND SEMICONDUCTORS BY PHYSICAL VAPOR TRANSPORT***

**DR. CHING-HUA SU
PRINCIPAL INVESTIGATOR
USRA STAFF SCIENTIST
CRYSTAL GROWTH AND SOLIDIFICATION PHYSICS BRANCH**

AUGUST 22, 1993

UNIVERSITIES SPACE RESEARCH ASSOCIATION (USRA)*
MICROGRAVITY SCIENCE AND APPLICATIONS PROGRAM

FINAL REPORT ON THE PRELIMINARY DEFINITION PHASE

**Crystal Growth of ZnSe and Related Ternary Compound Semiconductors
by Physical Vapor Transport**

Principal investigator: Dr. Ching-Hua Su, USRA Staff Scientist
Crystal Growth and Solidification Physics Branch
Microgravity Science and Applications Division
Space Science Laboratory/ES75
Marshall Space Flight Center, AL 35812
Tel. (205)544-7776
Fax: (205)544-8762

Co-Investigators:

Prof. Robert F. Brebrick
Materials Science and Metallurgy Program
Department of Mechanical Engineering
Marquette University
Milwaukee, WI 53233
Tel. (404) 288-1595

Dr. Martin Volz, Research Scientist
Space Science Laboratory/ES75
Marshall Space Flight Center, AL 35812
Tel. (205)544-5078

Dr. Yi-Gao Sha, Visiting Scientist
Universities Space Research Association
Space Science Laboratory/ES75
Marshall Space Flight Center, AL 35812
Tel. (205)544-7765

Dr. David Noever, Research Scientist
Space Science Laboratory/ES76
Marshall Space Flight Center, AL 35812
Tel. (205)544-7783

Industrial Guest Co-Investigators:
Drs. Sanghamitra Sen and Scott Johnson
Member of Technical Staff
Santa Barbara Research Center
75 Coromar Drive
Goleta, CA 93117
Tel. (805)562-2482, 562-2356

*USRA is a non-profit organization

1. SUMMARY

This work was a joint effort including participants from Universities Space Research Association (USRA), NASA Marshall Space Flight Center (MSFC), Marquette University Materials Science and Metallurgy Program, and Santa Barbara Research Center. Other contributors included Center for Photonic Materials and Devices, Department of Physics, Fisk University and Department of Materials Science and Engineering, State University of New York at Stony Brook.

The materials to be investigated are ZnSe and related ternary semiconducting alloys (e.g., $\text{ZnS}_x\text{Se}_{1-x}$, $\text{ZnTe}_x\text{Se}_{1-x}$, and $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$). These materials are useful for opto-electronic applications such as high efficient light emitting diodes and low power threshold and high temperature lasers in the blue-green region of the visible spectrum. The recent demonstration of its optical bistable properties also makes ZnSe a possible candidate material for digital optical computers.

The investigation consists of an extensive ground-based study followed by flight experimentation and involves both experimental and theoretical work. The objectives of the ground-based work are to establish the characteristics of the crystals grown on Earth as a basis for subsequent comparative evaluations of the crystals grown in a low gravity environment and to obtain the experimental data and perform the analyses required to define the optimum parameters for the flight experiments.

During the six months of the Preliminary Definition Phase, the research efforts were concentrated on the binary compound ZnSe - the purification of starting materials of Se by zone refining, the synthesis of ZnSe starting materials, the heat treatments of the starting materials, the vapor transport rate measurements, the vapor partial pressure measurements of ZnSe, the crystal growth of ZnSe by physical vapor transport, and various characterization on the grown ZnSe crystals.

2. OBJECTIVES AND RATIONALE

2.1 Overall Objectives

The objectives of the proposed investigation are the following:

- a) to determine the relative contributions of gravitationally driven fluid flows to the incorporation of impurities and defects and the deviation from stoichiometry (native defects) observed in the crystals grown by physical vapor transport due to irregular fluid-flows and growth interface fluctuations.
- b) to evaluate the effect of gravity on the vapor transport process by examining the compositional distribution of the ternary compounds grown in the process.
- c) to assess the relative amount of strain developed during processing at elevated temperatures caused by the gravitational weight of the crystals.
- d) to obtain a limited amount of high quality space-grown materials needed for various property characterization and device fabrication and thus assess the effect of microgravity on the device performance.

2.2 Objectives and Scope of Ground-Based Studies

The investigation consists of extensive ground-based experimental and theoretical research efforts and concurrent flight experimentation. The objectives of the ground-based studies are to (i) obtain the experimental data and conduct the analyses required to define the optimum growth parameters for the flight experiments, (ii) perfect various characterization techniques to establish the standard procedure for material characterization and to also quantitatively establish the characteristics of the crystals grown on Earth as a basis for subsequent comparative evaluations of the crystals grown in a low-gravity environment, and (iii) develop theoretical and analytical methods required for such evaluations.

The following are the specific tasks:

- a) Establish quantitative correlation between growth parameters (thermal fields, translation rates, vapor species, partial pressures, ampoule geometry, compositions and heat treatments of starting materials, and oriented seeded or unseeded conditions), growth interfaces shapes, compositional redistribution, densities and distributions of dislocations, impurities, small grain boundaries, second phase inclusions, twins, and other structural properties of the crystals grown by physical vapor transport.
- b) Evaluate the effectiveness of gravitationally driven convection in the growth process by performing experiments under various vapor transport orientations relative to gravitational direction (i.e., horizontal, vertically stabilized and destabilized configurations).
- c) Develop a theoretical model to delineate the effects of mass transport and heat transfer on the distributions of alloy composition, the structural defect (dislocation), the impurities, and the solid-vapor interface shapes during the process of physical vapor transport and compare the results with those obtained in (a) and (b) above and thus establish a fundamental understanding of the crystal growth process.
- d) Establish the partial pressure three phase curves of the vapor species in these system by measuring the optical absorption of the vapor phase coexisting with the condensed phases.
- e) Evaluate the fundamentals of the current vapor transport theories by performing measurements of the partial pressures of the individual species and the vapor transport rates simultaneously.
- f) Perform opto-electronic characterization and thus establish the correlation between the electrical and optical characteristics of the grown crystals and the processing parameters.
- g) Evaluate the potential benefits of microgravity processing for device applications by means of fabricating devices from both ground- and space-grown materials.

3. MATERIALS

3.1 Materials Selected

The materials to be investigated are ZnSe and related ternary semiconducting

alloys such as $\text{ZnS}_x\text{Se}_{1-x}$, $\text{ZnTe}_x\text{Se}_{1-x}$, and $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ because of their potential for advanced opto-electronic applications. With an energy gap of 2.7 eV at room temperature, ZnSe has been studied extensively [1] as the primary candidate for blue light emitting diode applications because of its efficiency in band-to-band transitions. It has been found in the last several years that ZnSe bulk crystals [2] and heterostructures such as ZnSe/ZnSSe [3], ZnSe/ZnCdSe [4], and ZnCdSe/ZnSSe [5] showed photopumped lasing capability in the blue-green region at a rather low threshold power and high temperature. On the other hand, the recent demonstration of the optical bistable properties in bulk [6] and layer [7] ZnSe also makes ZnSe a possible candidate for the building blocks of a digital optical computer.

3.2 Rationale for Material Selection

Interest in optical devices that can operate in the visible spectrum has motivated recent research interest in II-VI wide band-gap materials. ZnSe is especially attractive because the band gap of this materials is suitable for blue light emitting devices for use in optical displays, high density recording, and military communications. Efficient light emitting diodes based on single crystal ZnSe have been reported [8]. The recent challenge of semiconductor opto-electronics is the development of a laser at short visible wavelengths. While issues related to the compositional inhomogeneity and defect incorporation are still to be fully resolved, ZnSe and related semiconducting alloys have been studied in optically pumped lasing experiments in the blue region of the spectrum [2-5]. A major constraint in the exploitation of ZnSe is still the lack of high quality substrates on which high quality epitaxy can be achieved. Adding another element to ZnSe to form the ternary compounds, such as $\text{ZnS}_x\text{Se}_{1-x}$, $\text{ZnTe}_x\text{Se}_{1-x}$, and $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$, gives tunability to the energy band gap so as to cover a wider range of the visible spectrum. Figure 1 shows the band gap energy as a function of x in $\text{ZnS}_x\text{Se}_{1-x}$ [9], $\text{ZnTe}_x\text{Se}_{1-x}$, and $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ systems [10]. The wavelengths correspond to the energy gap curves are shown on the right scale. By changing the amount of S, Te, or Cd added into ZnSe one can cover the visible spectrum from near red through yellow, green, to blue.

The other potential application which has not been studied extensively is the optical bistable characteristics of ZnSe [6,7] which exhibited a non-linear abrupt change in optical absorption for increased light intensities. This property addresses a basic requirement for the optical switches used in digital optical computers.

4. Experimental and Analyses

4.1 Purification of Starting Se materials:

a) work performed: A zone refiner was set up. It consists of two traveling ring heaters inside a box furnace. The distance between the two heaters is 36.5 cm and the total travel distance is 48 cm. The furnace axis is at an angle of 10° to the horizon. The temperature settings for the ambient, left and right zone heaters were, respectively, 220, 380 and 380°C . Figure 2 shows the thermal profiles near the left zone heater. Since Se melts at 217°C , the zone length of the melt was roughly 2.5 cm. A fused silica ampoule (17mm OD, 14mm ID) was cleaned and baked out at 1000°C under vacuum condition overnight. The starting material was 99.999% grade, 1/8" dia. shots Se from Cerac Corp. A total amount of 150.314 g was loaded in the ampoule and the Se was melted under vacuum before the ampoule was sealed under vacuum condition. The zone

Band Gap of ZnSeS ZnSeTe and ZnCdSe

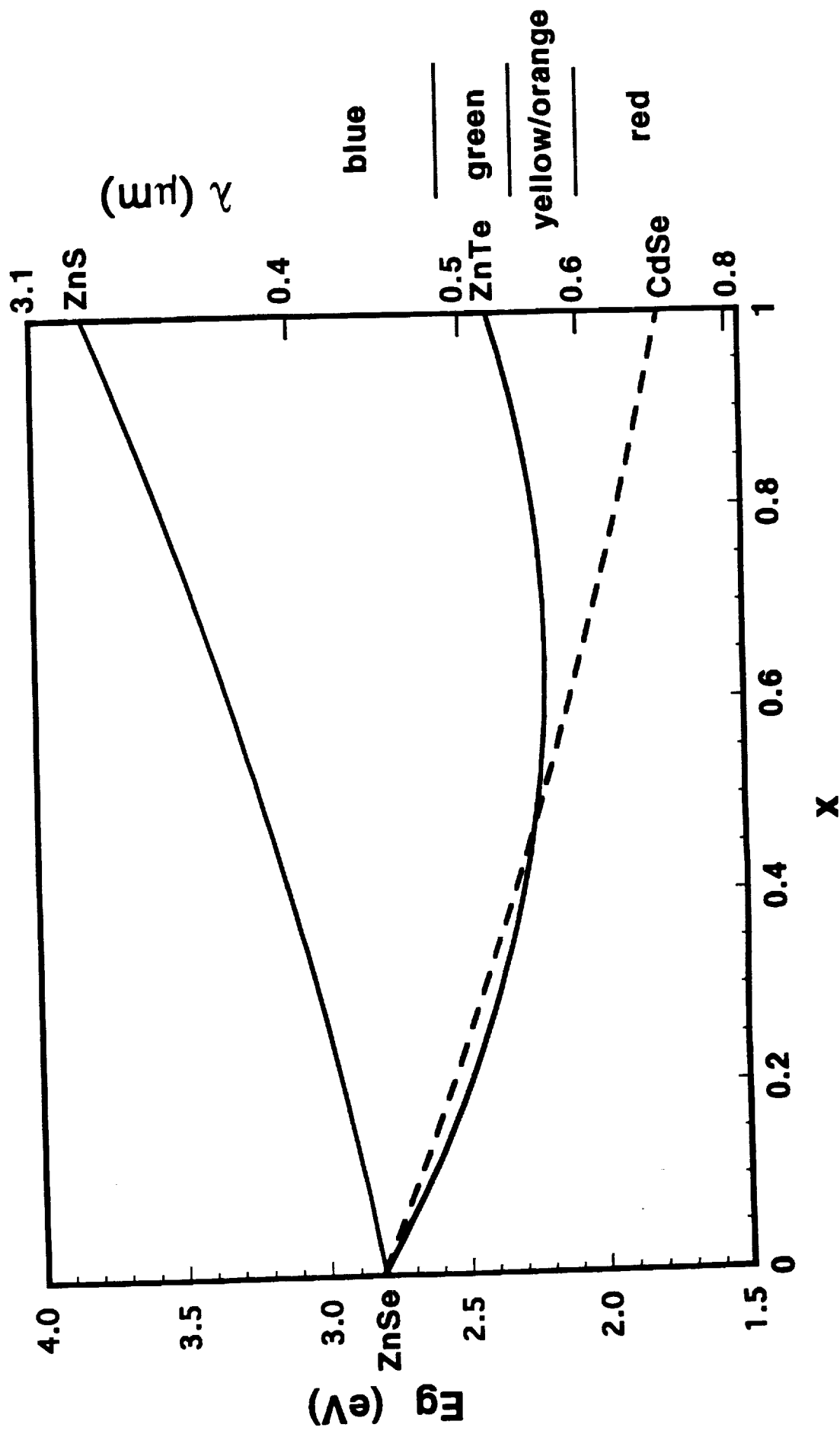
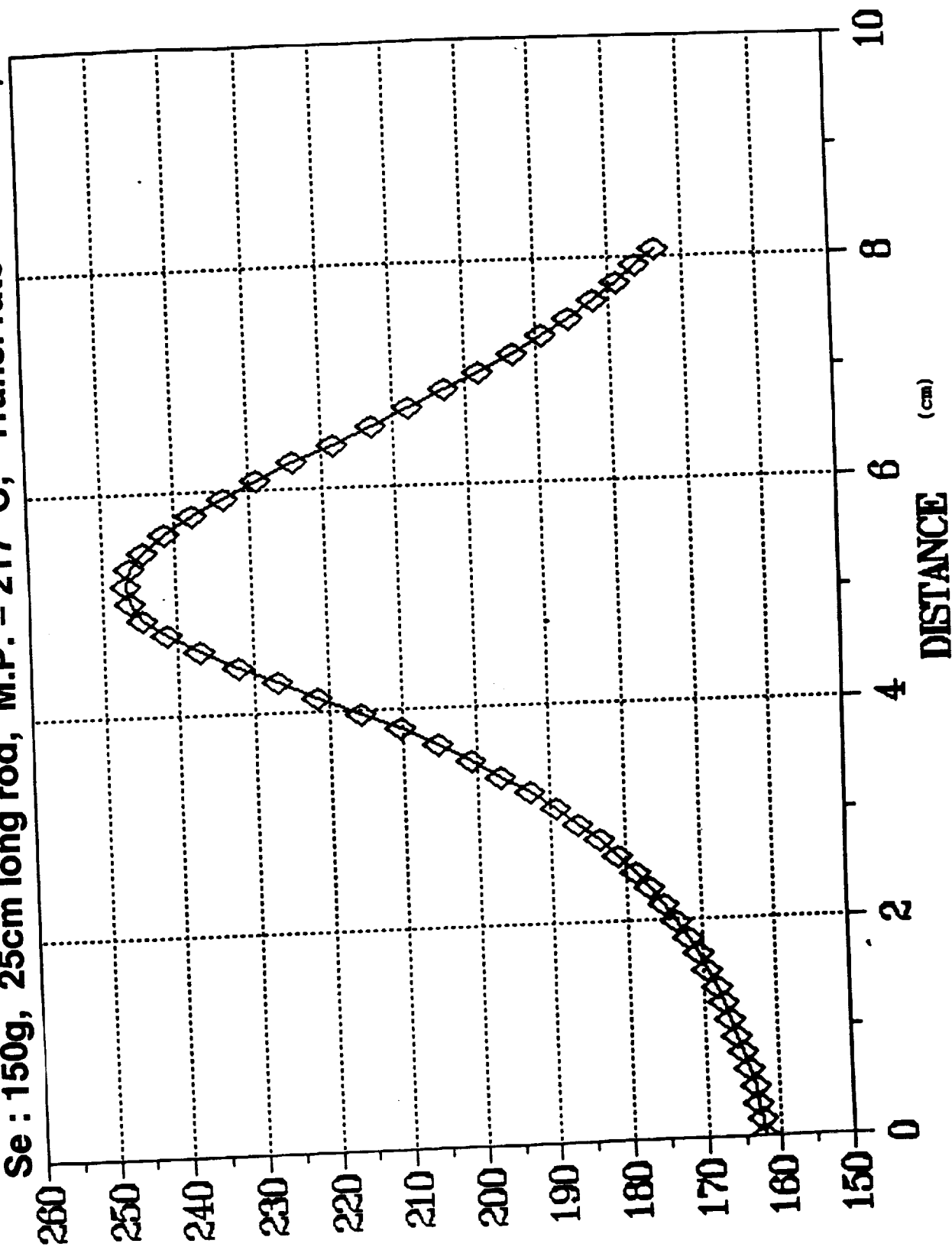


Figure 1

Se : 150g, 25cm long rod, M.P. = 217 °C; Trans. rate = 1.91 cm/hr



◇ TEMP

Figure 2

heaters were automated to translate at slow speed when moving toward the lower end until they have reached the end of travel then translate fast toward the upper end of the furnace and continue for the next cycle. The translation rates were 1.91 cm/hr and 540 cm/hr for the slow and fast translation, respectively. The zone refining process was stopped and furnace turned off after 10 translational cycles or 20 zone passes. At positions corresponding to 0, 0.25, 0.5, 0.75 and 1.0 of the total ingot length, five slices were cut and sent to Walters Chemical Consultant Co. for chemical analyses to study the effectiveness of the zone refining process. The results of the spark source mass spectrographic analyses of the five slices are shown in Figures 3 and 4. Except Si, the impurity levels of all the elements are below 10 ppm and although the impurity distributions along the ingot follow the theoretical trend of a zone refining process the effectiveness of purification is somewhat lower than expected.

b) work to be performed: Another zone refining process will be performed with more zone passes to examine the effectiveness of the purification.

4.2 Synthesis of ZnSe starting materials:

a) work performed: Two cylinders of zone-refined Se (cut from the middle section of the zone-refined ingot) were first degreased by immersing in trichloroethylene at about 60°C for 20 min and cleaned with an ultrasonic cleaner in acetone, methanol and distilled water. The Se ingots were then etched in 70% nitric acid for 30 sec, rinsed with distilled water and cleaned with an ultrasonic cleaner in distilled water. The ingots were then dried by blowing with high purity argon gas. The Se ingots were ground into small chunks with mortar and pestle. 22.31 grams of Se and 18.47 grams of Zn (69 grade from Johnson Matthey) were loaded into a pre-cleaned, out gassed ampoule for synthesis. The synthesis ampoule (ZnSe #1) was heat treated at 1080 °C for 4 days and then at 1010 °C for 25 days. The material in the middle section of the ampoule showed yellow-orange color but the materials at two ends of the ampoule were still black in color and some black chunky condensation could be seen at the right end of the ampoule.

b) work to be performed: More heat treatment will be done on ampoule ZnSe #1.

4.3 Heat treatment of starting materials:

In the physical vapor transport process the transport rate is at its maximum when the source material sublimates congruently, i.e., the vapor phase has the same composition as the solid phase [11]. Because vapor partial pressures coexisting with the solid phase depend strongly on the small deviation from stoichiometry of the solid, it is almost impossible to reproducibly weigh out the amount of elements to form the compounds that have certain values of partial pressures. One method to adjust the stoichiometry of the starting materials, which makes the samples sublime more congruently, is to bake out the materials under dynamic vacuum condition [15]. The change in stoichiometry stops when the materials sublime congruently. The other method is simply the distillation of the materials. The purpose of the heat treatment process, together with vapor partial pressure measurements, is to reproduce the same stoichiometry - as close to congruent sublimation as possible - for the source materials so that the transport rate is the highest and the same during each growth run.

a) work performed: All the ZnSe starting material used in the six-month period was from Cleveland Crystals, Inc. with purity of either 99.995% or 99.999%. The starting materials were treated in one of the following two methods before sealed off. (1) the

Impurity Distribution of Zone Refined Se Ingot
(22cm long, 14mm diameter)

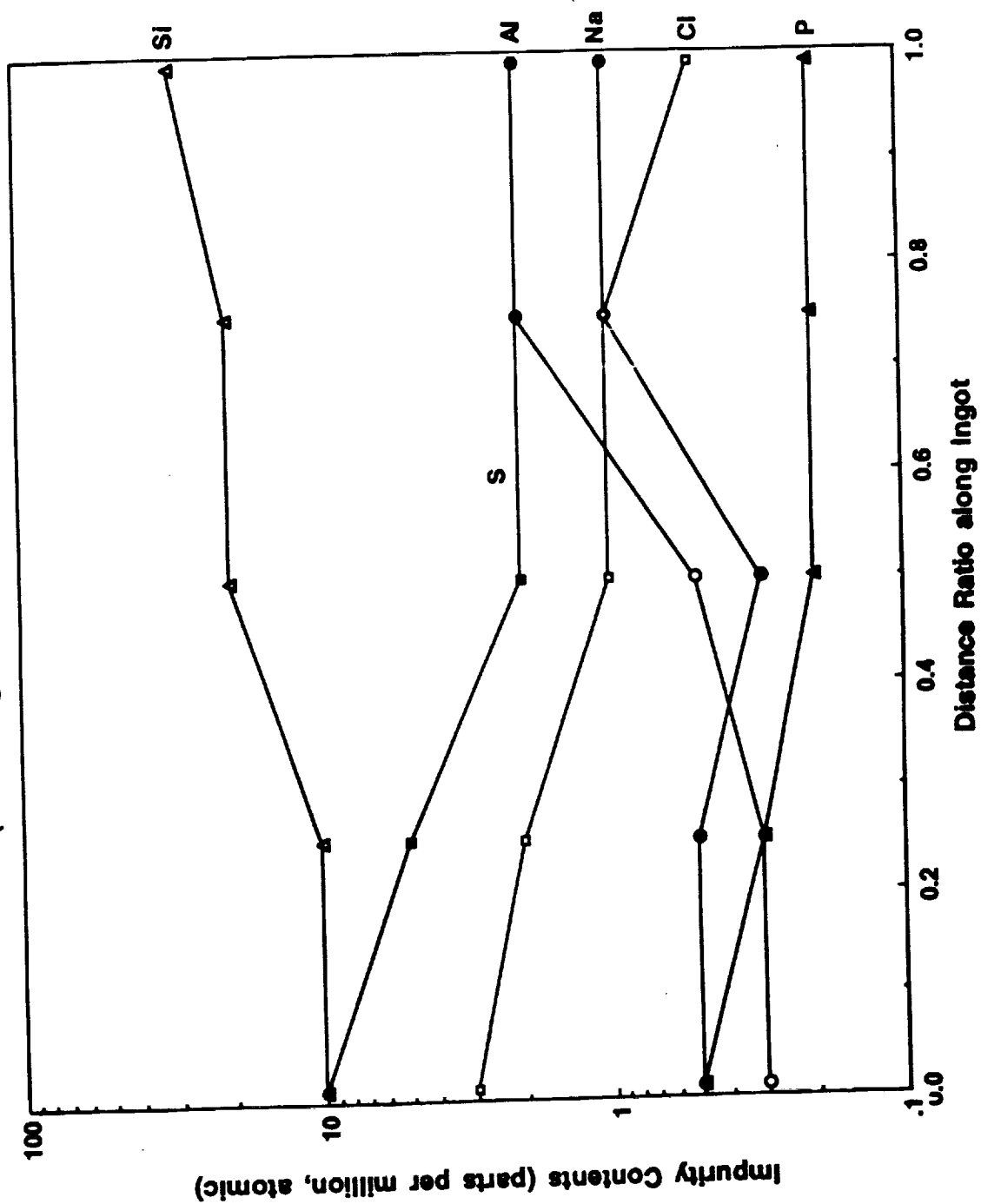


Figure 3

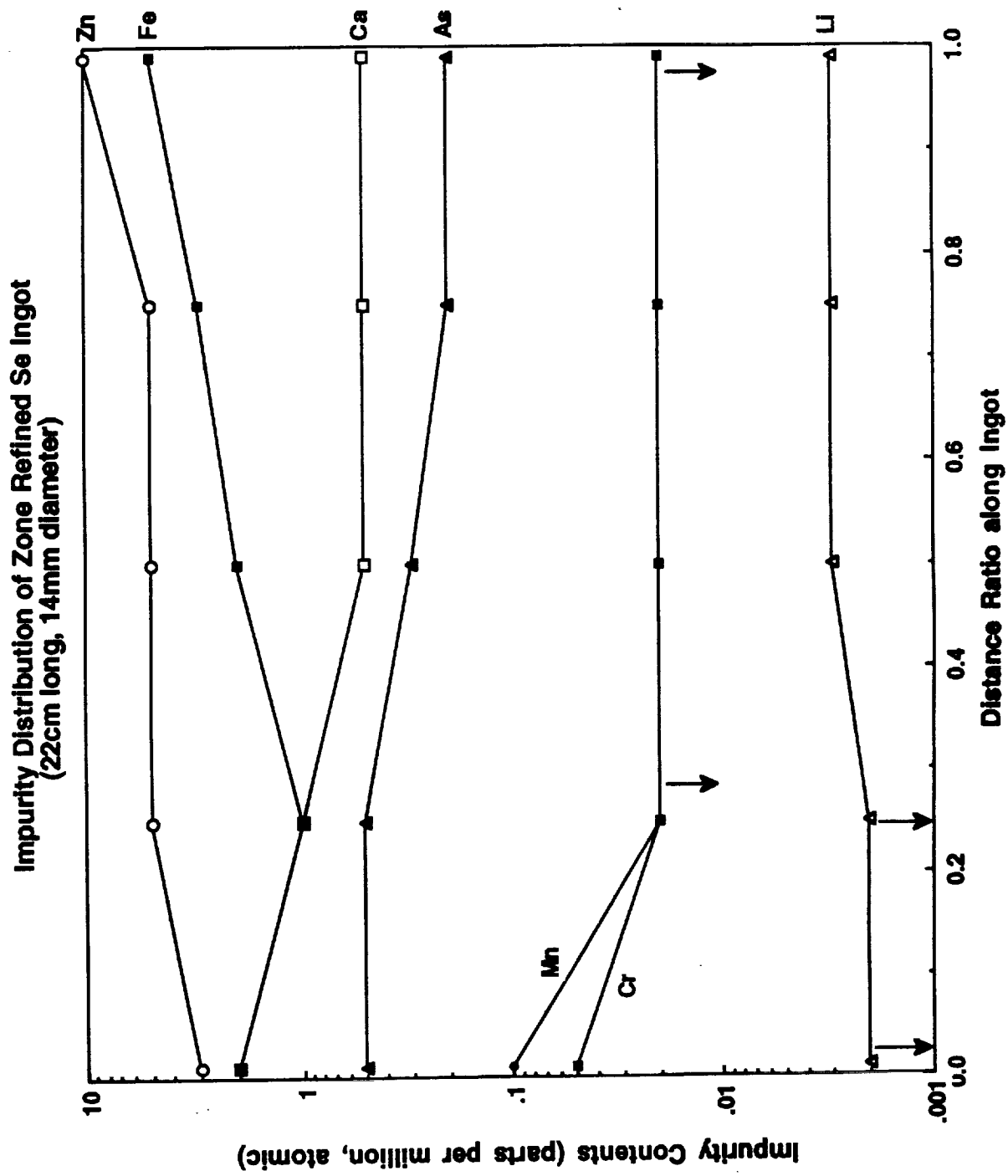


Figure 4

material was baked out at about 1080°C under dynamic vacuum condition for about 10 min or (II) the material was distilled by subliming it from one end of the ampoule and depositing it on the other end under dynamic vacuum condition. A schematic of the set-up is shown in Figure 5. The subliming temperature was about 1080°C and the thermal barrier which confined the condensation of the material to a narrow region was about 800°C. At the end of the distillation most of the starting ZnSe was transported. However, in one occasion when 99.995% pure ZnSe was used as starting material there was a small white chunk left at the end of the process. By Energy Dispersive X-ray analysis (EDX) the main constituents of the white material were identified to be Zn and O.

b) work to be performed: It is critical to have the highest transport rates reproducibly in every crystal growth process. A standard procedure for method (b) will be established to accomplish this goal.

4.3 Transport rate measurements:

a) work performed: A three-zone clam shell furnace was set up to conduct the transport rate measurements. The schematic of the set-up is illustrated in Figure 6. A transport ampoule, ZST -2, contains about 2 g of ZnSe heat treated by method (II) was prepared. The temperatures at the source, T_s , and at the deposit, T_d , were 1070 and 1063°C, respectively. The readings of the balance were recorded manually and the transport rate plotted in Figure 7. About 25 hr into the run the right zone of the furnace was out of control and the run was terminated. The furnace was repaired later and the run continued. The baseline for the second set of data shown in Figure 7 has been adjusted so that the total amount of materials transported matches the amount loaded. The transport rates for the two sets of data were estimated and plotted in Figure 8. After 25 hr into the run the transport rate can be approximated as a constant of 1.27×10^{-8} (mole/cm² sec). The measurement was automated by procuring a Mettler AE100 balance with digital output capability. Another ampoule, ZST -4, containing about 1.5 g ZnSe heat treated by method (b) was prepared. Figure 9 shows the ZnSe transported as a function of time. Data were taken at 30 min interval. During the course of the measurement, the temperatures of T_s and T_d drifted up. However, the temperature difference remained almost constant at 14°C. Constant transport rates were approximated for three different segments and are plotted in Figure 10. A second run was performed on ampoule ZST - 4 by reversing the temperature profile of the furnace so that the material transported from the deposit end back to the source end. The raw data are shown in Figure 11 and the curve can be approximated by a second-order equation. The calculated transport rates from this equation together with the results from the first run are given in Figure 12. There are three things worth noting. First, the transport rates were not constant throughout a run because the stoichiometry of the source kept changing during the run as material of different composition deposited at the other end. Second, the increase in $T_s - T_d$ from 14 to 20°C in run 2 did not show much effect on the measured transport rates. This implies that transport rates might have reached saturation for a $T_s - T_d$ of 14 °C. Third, an Arrhenius graph obtained by plotting the logarithmic of the transport rates against $1000/T_d$ is close to be a straight line as shown in Figure 13 and it predicts that the transport rate at 1106°C is about 10 times higher than that at 1060°C. The results from ZST -2 and ZST -4 were not compared because the stoichiometry may be different for these two ampoules although they were prepared by the same technique.

b) work to be performed: All the materials inside the transport ampoule will be

Illustration for Heat Treatment of ZnSe Starting Materials

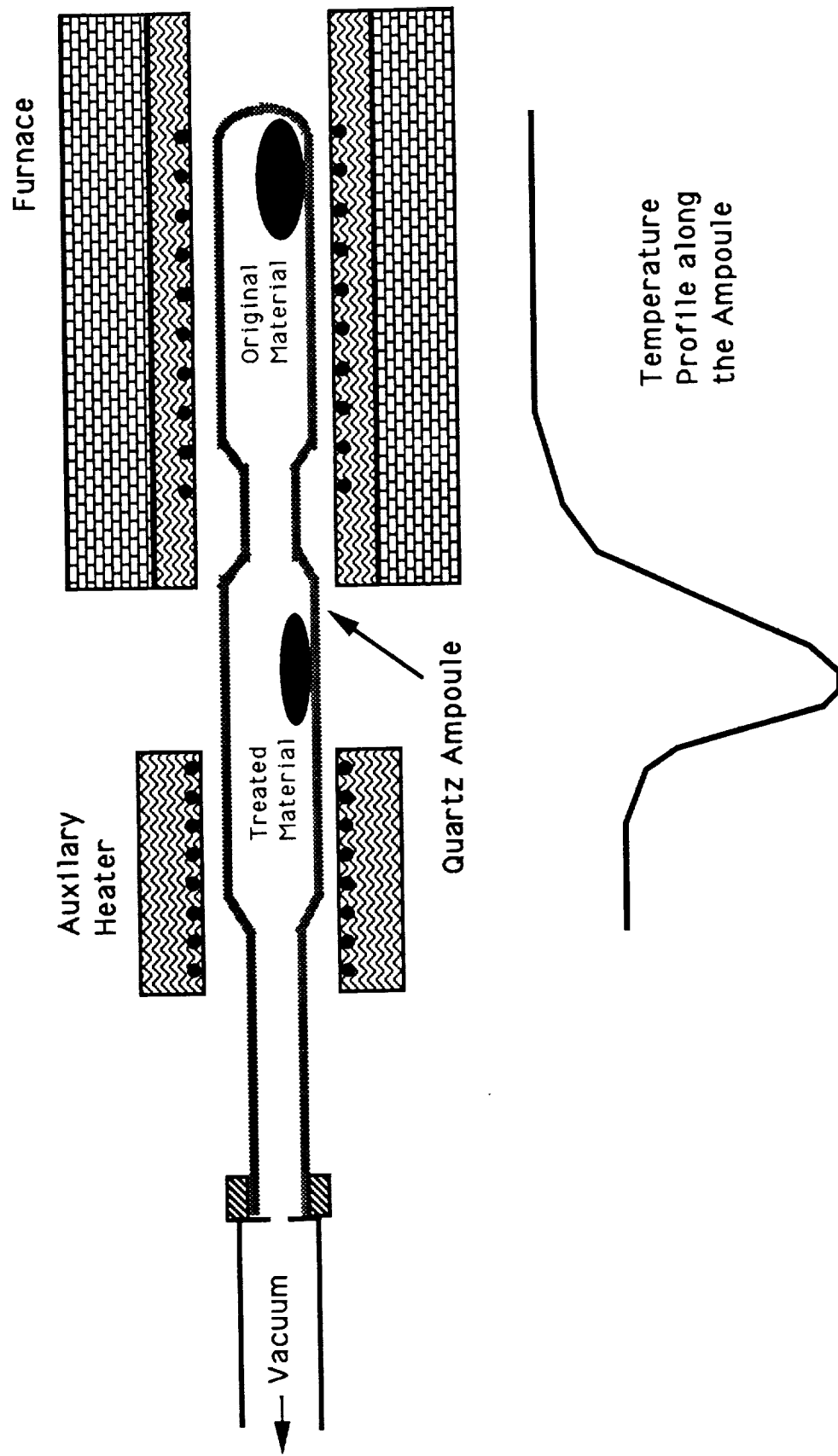


Figure 5

Illustration for Transport Measurement of ZnSe

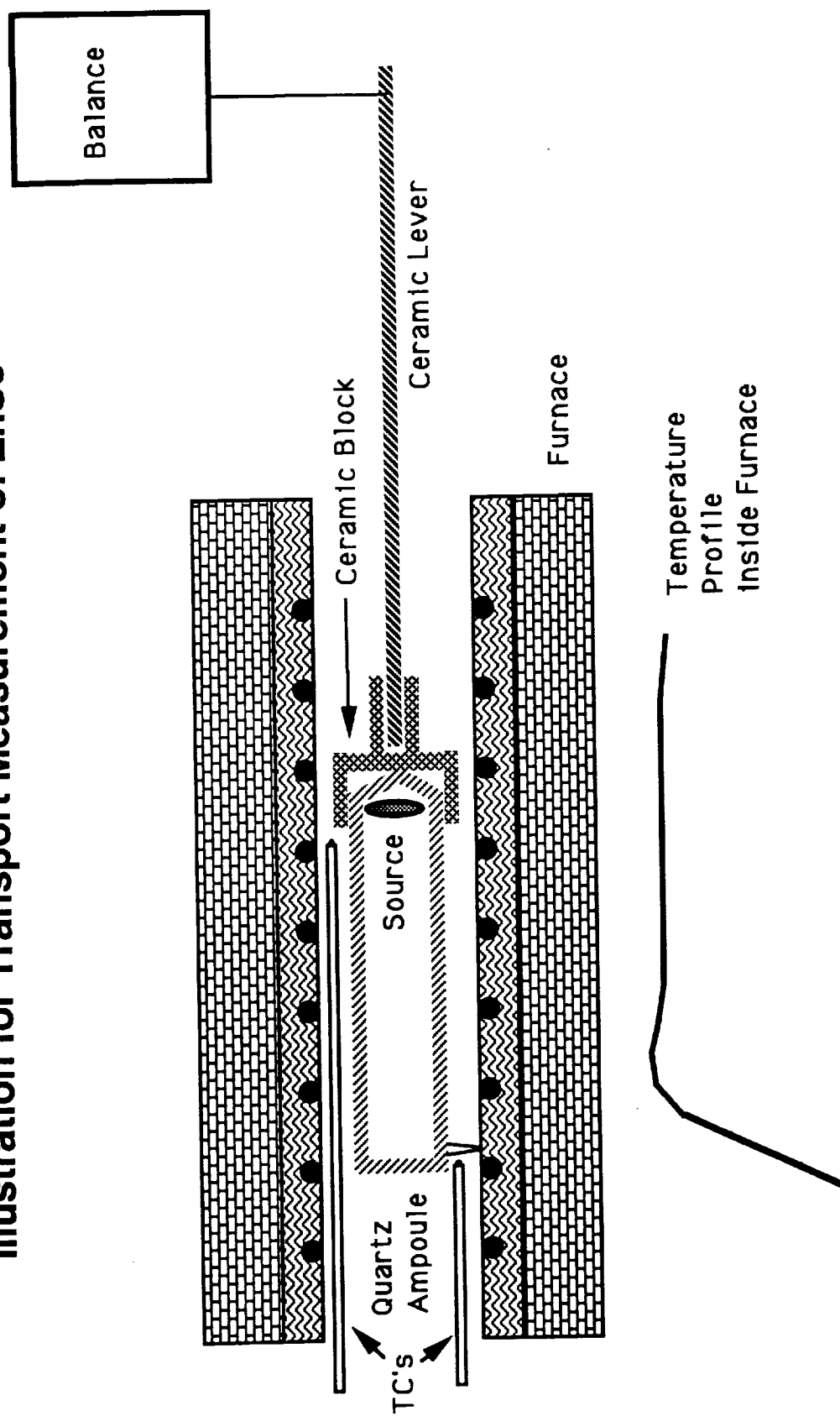


Figure 6

ZnSe Transport Results (ZST-2) with baseline correction

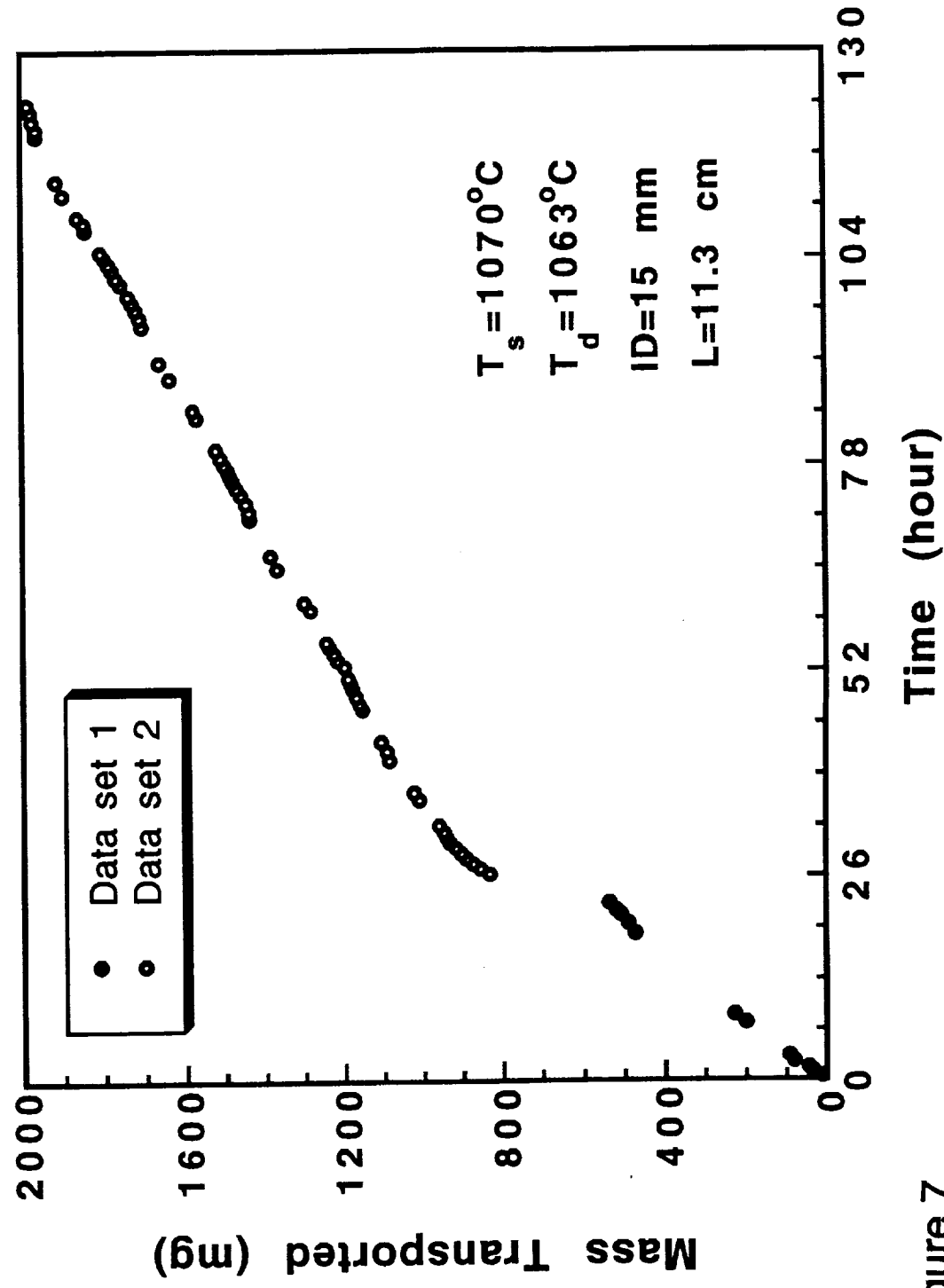


Figure 7

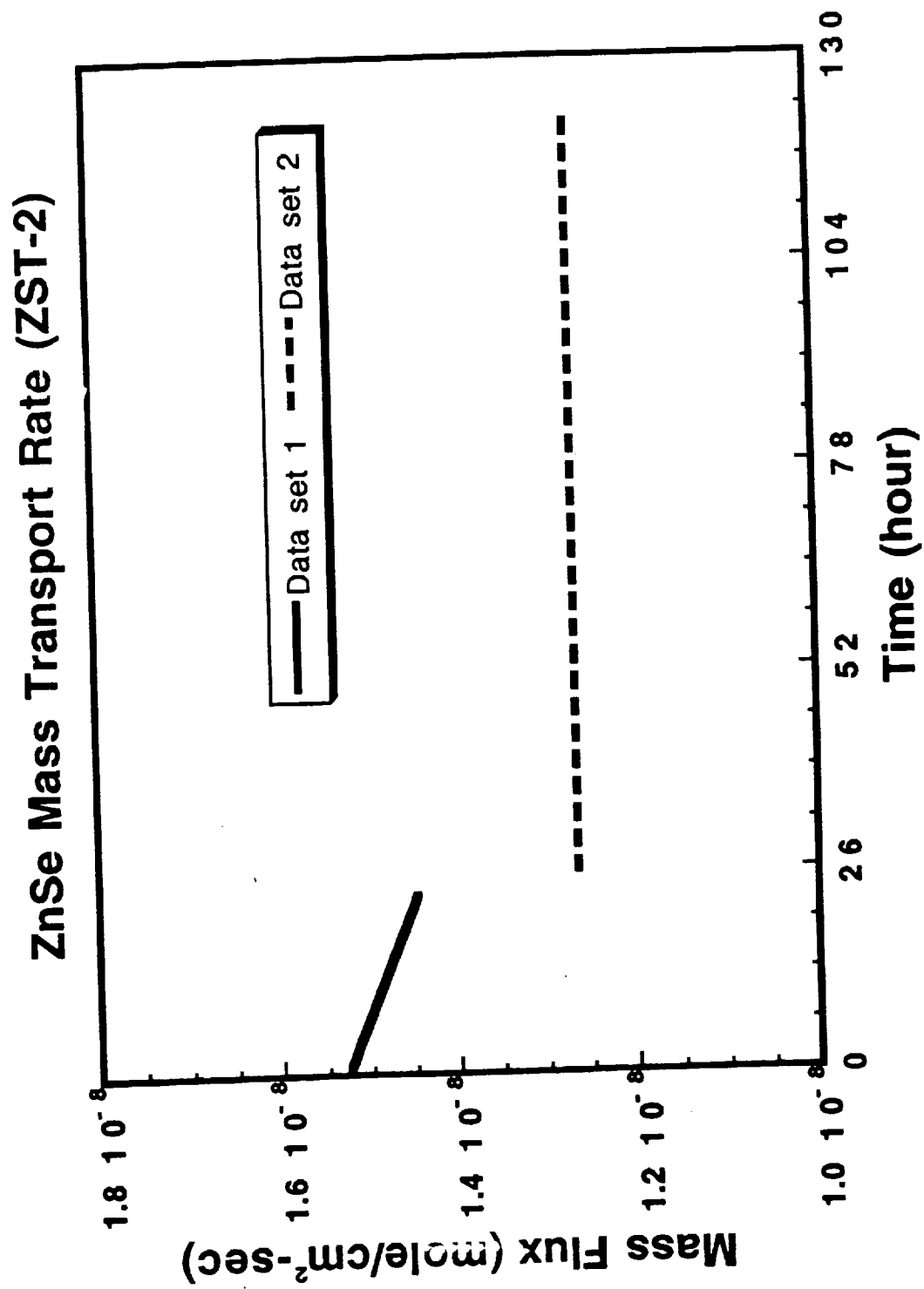


Figure 8

ZnSe Transport Results (ZST-4)

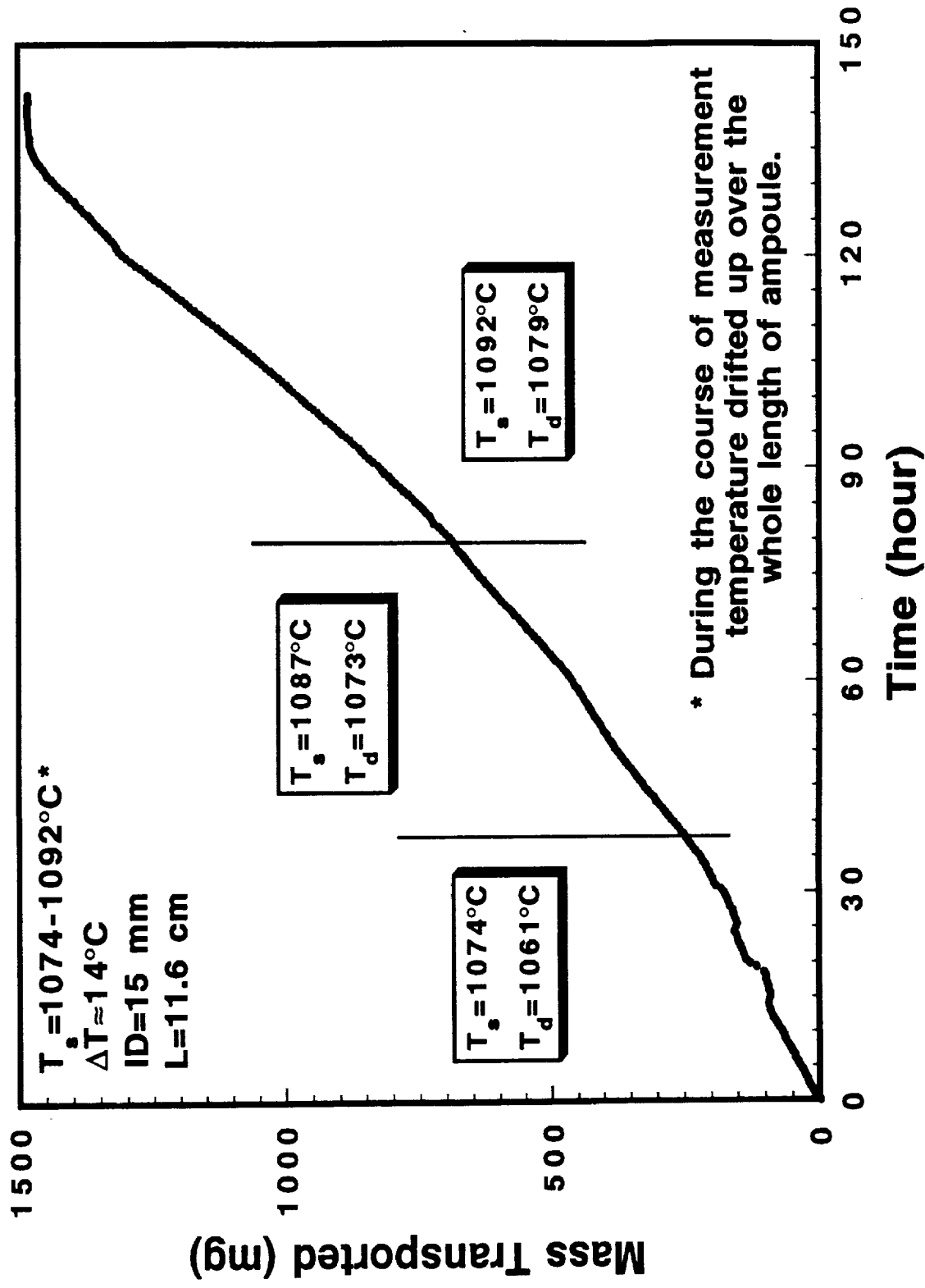


Figure 9

ZnSe Mass Transport Rate (ZST-4)

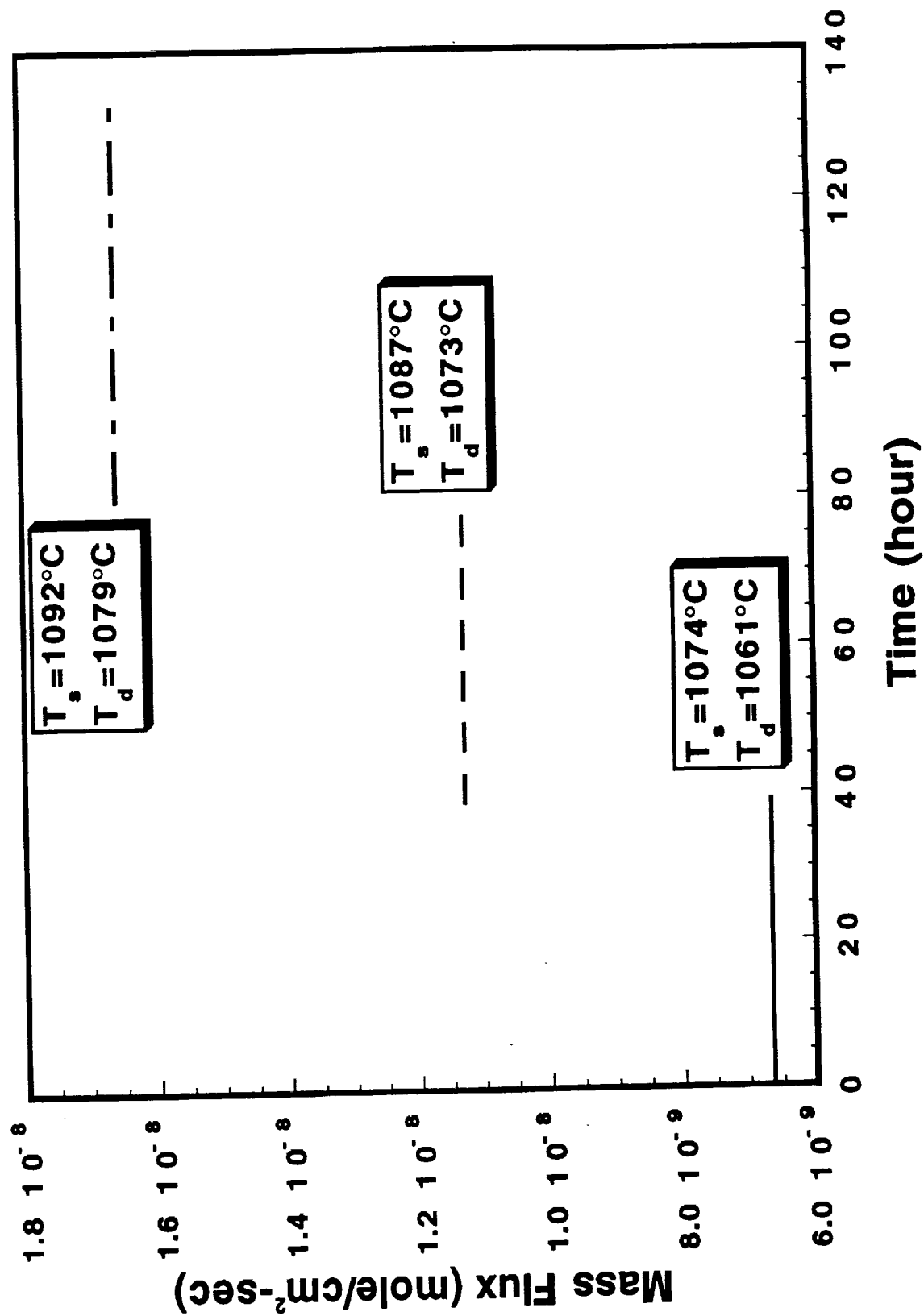


Figure 10

ZnSe Transport Results (ZST-4, run 2)

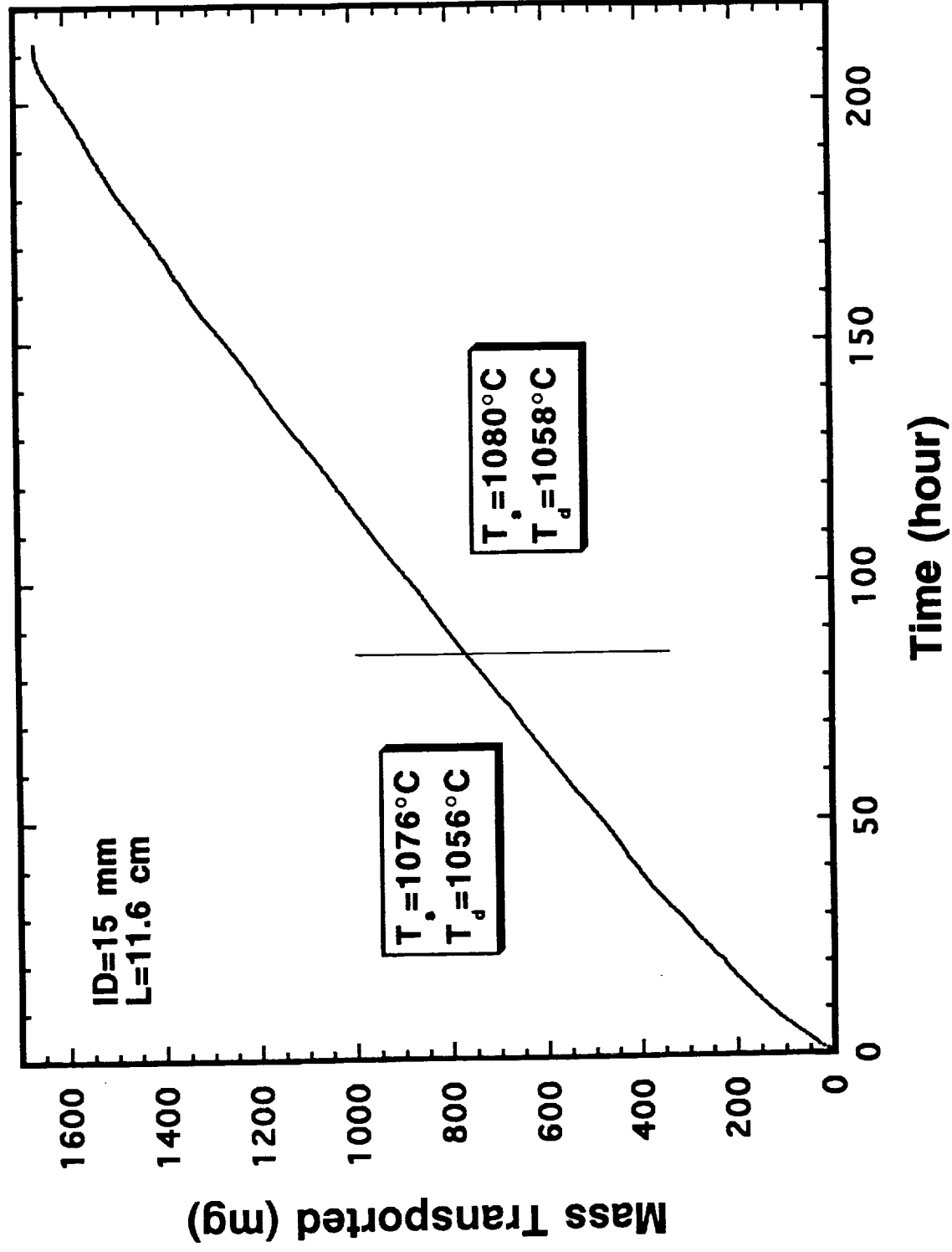


Figure 11

ZnSe Mass Transport Rate (ZST-4)

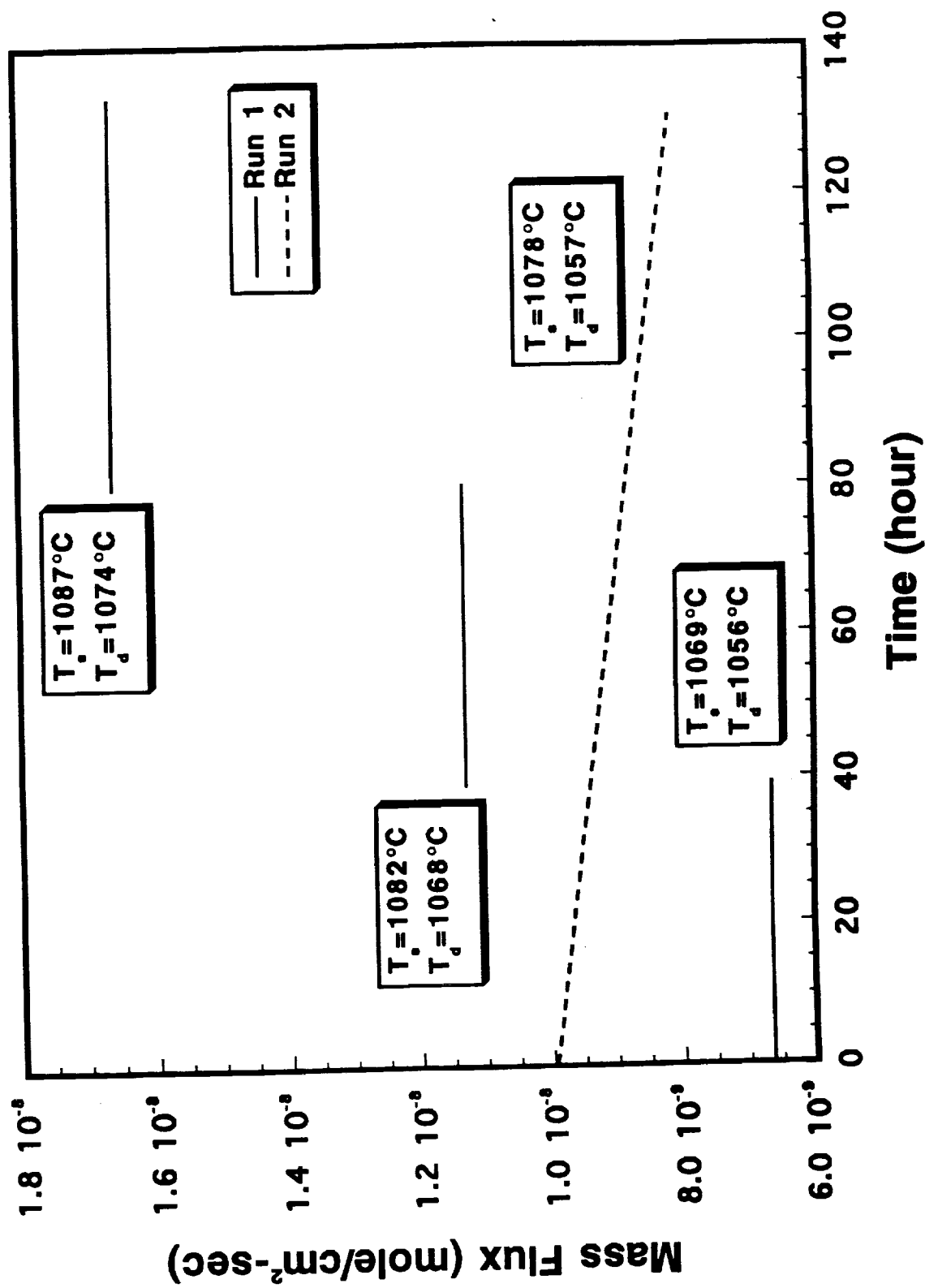


Figure 12

ZST-4

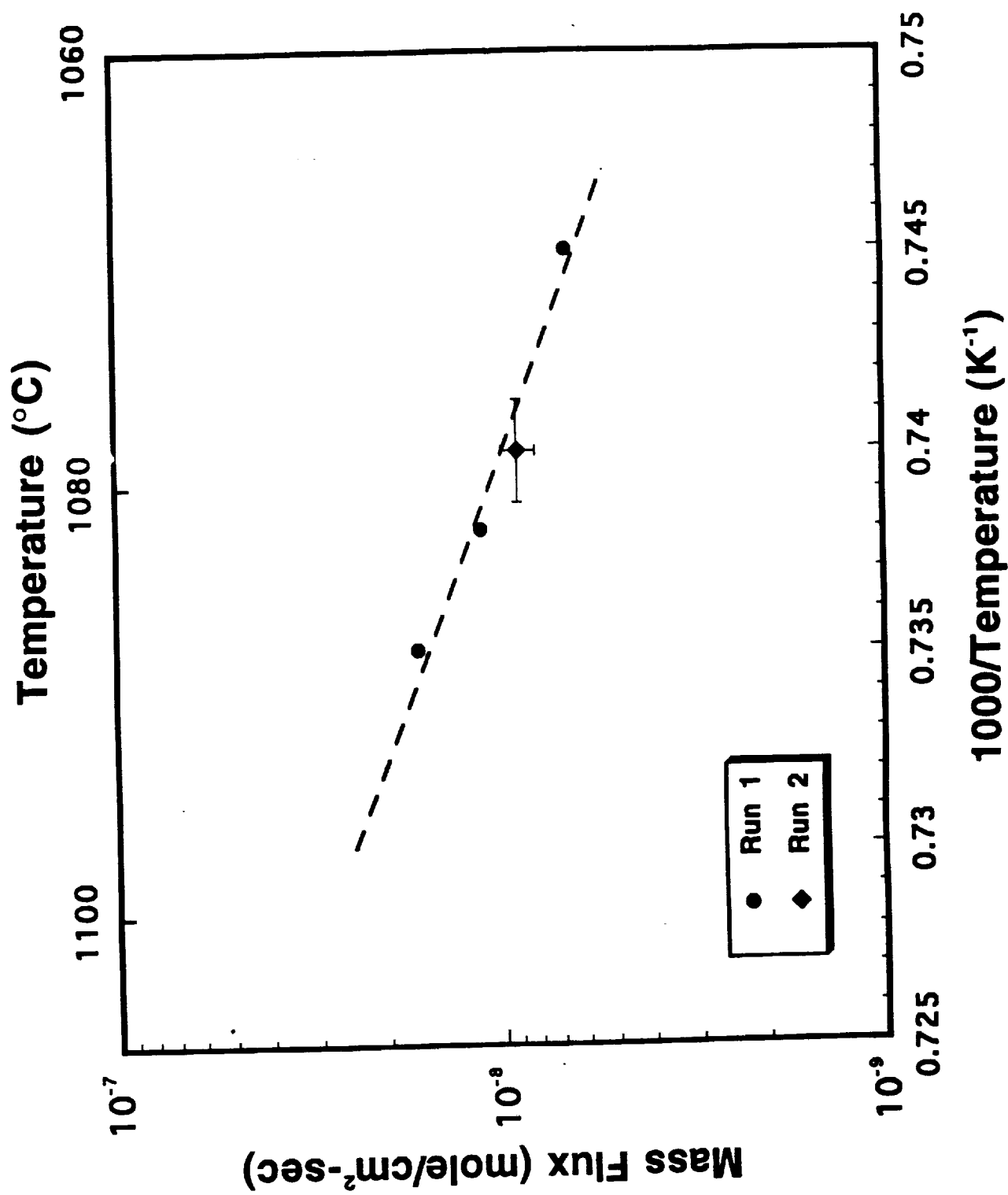


Figure 13

collected and loaded into an optical cell and the stoichiometry of the materials will be determined by partial pressure measurements at Marquette University. We will also measure the partial pressures and the transport rates simultaneously for the actual ampoules used in the growth transport experiments as described in next section.

4.4 Vapor partial pressure measurements:

a) work performed: Using an optical absorption technique [12], Brebrick and his coworkers at Marquette University have accomplished the following tasks:

1) Se calibration run: With optical cell temperatures of 1000°C and 1100°C and pure Se(l) temperatures between 206 and 400°C, the optical density of the vapor phase has been measured with a 0.4 nm band-pass between 200 and 220 nm, between 330 and 380 nm and near 450 and 496 nm. The range of total Se-pressures covered was about 5×10^{-6} to 7×10^{-3} atm. As expected the vapor in the optical cell is essentially all Se_2 . Between 200 and 220 nm, where higher species such as Se_5 absorb, the optical density was near the 0.01 minimum value measurable. Between 330 and 380 nm, vibronic peaks of Se_2 were seen and the optical density of those at 340.5 and 379.2 nm vary linearly with the partial pressure of Se_2 . More precisely, a plot of the log of the optical density vs. the reciprocal temperature of the liquid Se sample has the same slope as does the vapor pressure of Se. It is inferred from the thermodynamic data for Se-vapor in Mills [13] that the vapor was all Se_2 in both the 1000°C and 1100°C optical cells. Near 452 and 496 nm the optical density was below 0.01 and could be used to monitor shifts in the baseline. The optical density was also measured with an 800°C optical cell and 0.4 nm band-pass for Se(l) temperatures between 420 and 670°C, corresponding to total Se-pressures between 0.012 to 0.79 atm. The wavelengths covered were 410 to 455 nm, 590 to 610 nm, and 690 to 710 nm. At the highest liquid Se temperature of 670°C, the optical density was greater than the equipment maximum measurable value of 2 at all wavelengths from 200 to 710 nm.

2) Zn calibration run: Previous experiments have indicated that the optical density at the 213.8 nm Zn peak can be accurately calculated assuming a Voigt line profile and a triangular slit function. The experiments were carried out with optical cell temperatures of 1000, 950, and 750°C and band passes of 0.2 and 0.4 nm. Therefore the necessary relationships between the optical density at 213.8 nm and the partial pressure of Zn for optical cell temperatures of 1050 and 1100°C have been calculated.

3) ZnSe run: Partial pressures over a 50 mg sample of ZnSe (Cleveland Crystals, 99.999%) ground to pass a standard 120 urn sieve have been determined from the optical densities at 213.8, 340.5 and 379.2 nm with optical cell temperatures of 1000, 1050, and 1100°C. At the highest ZnSe temperatures allowable, about 10°C below the optical cell temperature, the time to achieve a steady state was a few hours and the optical densities were 0.3 and lower. As shown in Figure 14, the partial pressure of Zn is somewhat larger than twice that of Se_2 . Figure 15 shows the published data give results in agreement with our values for the Gibbs energy of formation of ZnSe.

b) work to be performed: It has been well established theoretically [11,14] that the vapor transport rate is a strong function of the vapor phase composition. However, no one has done any transport rate measurements with known vapor compositions to support the theoretical results. Here we propose to measure the partial pressures and

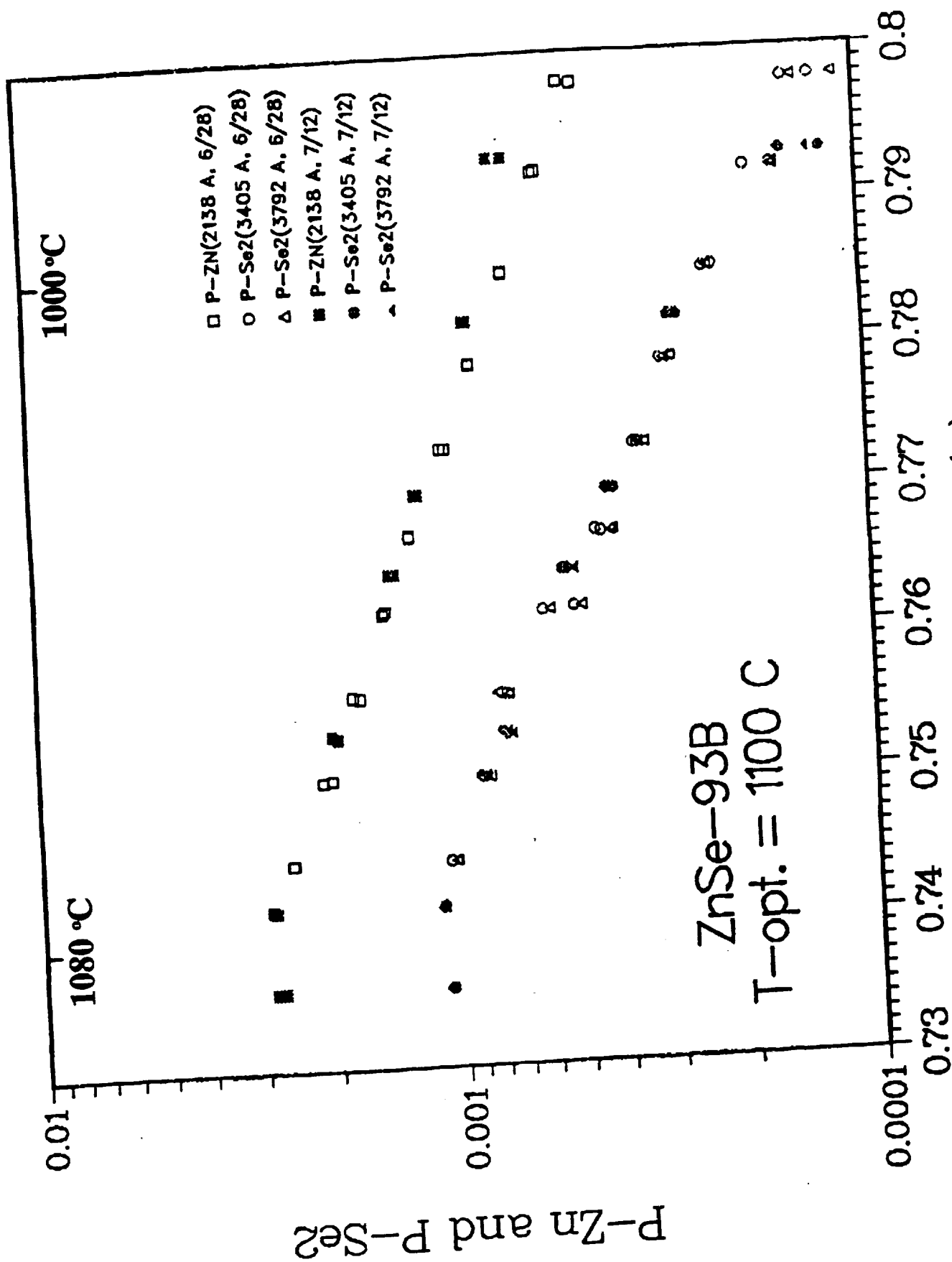


Figure 14

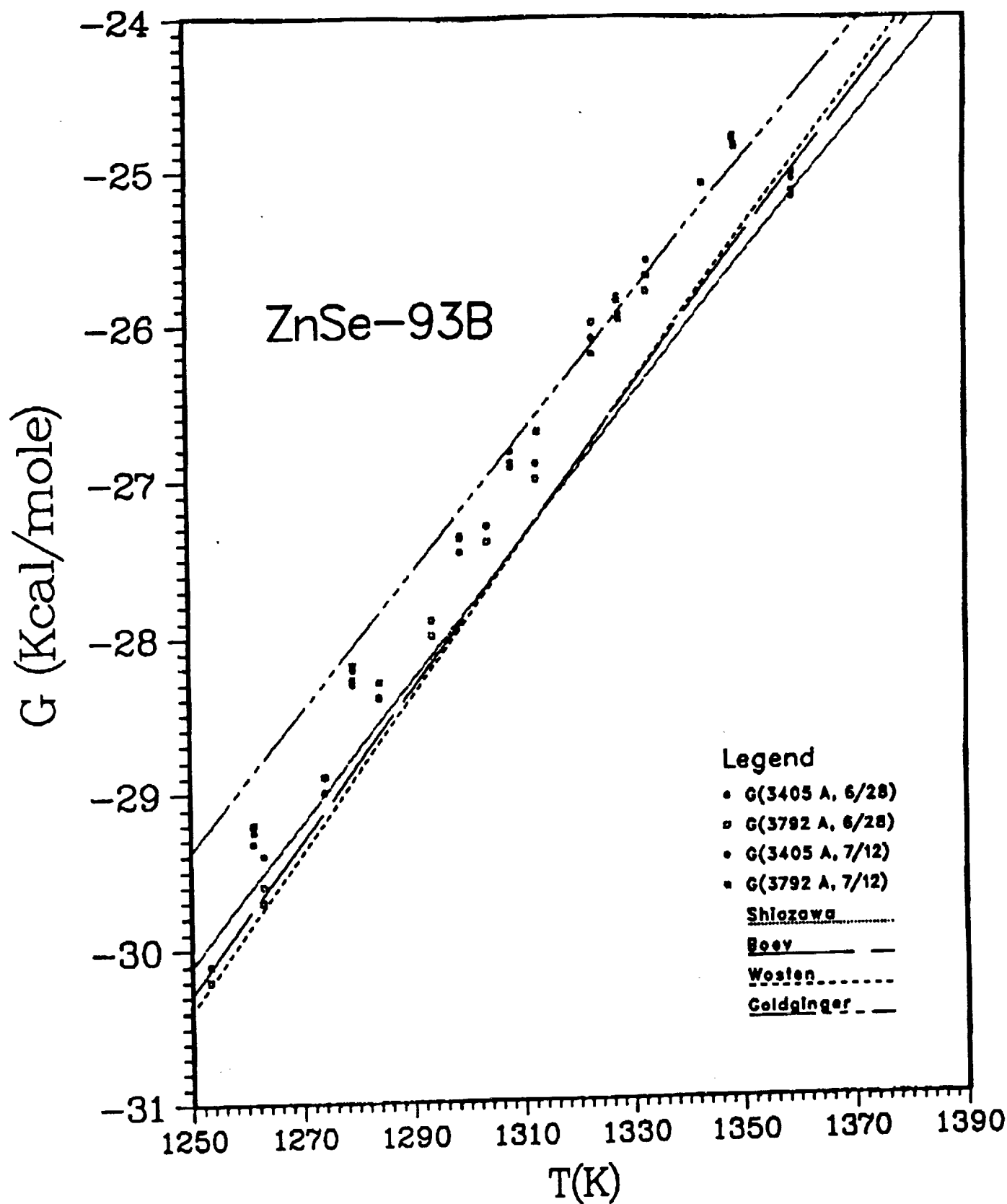


Figure 15

the transport rates simultaneously for the actual ampoules used in the growth experiments. Figure 16 shows the design of a such ampoule. The ampoules will be sealed after the samples have been heat treated under various conditions. The partial pressures coexisting with the sample will be determined by measuring the optical absorption of the vapor phase through the optical windows. At the same time the ampoule will be under a temperature gradient and the mass flux will be measured by a balance as described in last section which gives the amounts of mass transported at different time intervals. The results will be significant in that it will give support and guidance to the theoretical interpretation because, for the first time, vapor transport rates with known vapor compositions will be available in the physical vapor transport process.

4.5 Crystal growth experiments:

The crystal growth by physical vapor transport uses a novel three-zone heater translating technique. A schematic of the growth furnace is given in Figure 17. Using this method, large single crystals of CdS [15], CdTe, PbSe [16] and ZnTe [17] have been grown successfully in this laboratory.

a) work performed: The ampoules are made from TO8 grade tubing from Heraeus Amersil. They were cleaned and baked at 1080°C under vacuum over night before the samples were loaded. The ampoules were 18mm OD, 16mm ID, about 10cm long and with a tapered end. Four ampoules, ZnSe-1, -2, -3 and -4, loaded with the starting materials heat treated by method (I) - baking out under dynamic vacuum, were processed to grow ZnSe crystals with the source material at 1081°C, the cold end at 973°C and a temperature maximum in between of 1086°C. The translation rates were 3.19mm/day for ampoules ZnSe-1, -3, and -4 and 3.25mm/day for ZnSe-2. For ampoule ZnSe-1, only little specks of ZnSe transported and several thin layers of white semitransparent material can also be seen at the tip of the crystal end. For ampoule ZnSe-2, crystals of irregular shape covering about 1.6 cm were found at the crystal end and having rather red color as compared to the yellowish color of the starting material. A stable growth interface was never established. In the run of ZnSe-4, only a very thin film deposited at the tip. All three ampoules were foggy inside after the run. For ampoule ZnSe-3, only a small cone-shaped film (5 to 10 mm) was transported. However, the ampoule was not foggy. The interpretation is that somehow the ampoules were contaminated either from the source materials of ZnSe or originated from the fused silica ampoules after long duration annealing at high temperatures. In the ZnSe-5 and -6 runs, the heat treatment method (II) - distillation described in 4.3 was used. Figure 18 shows the thermal profile used for these runs. During the ZnSe-5 run, the outside fused silica liner sagged in the middle and the furnace dragged the whole liner with it when translating. The net translation was only 9mm. However, a single crystal with facets on the surface was grown and the furthestmost growth interface is at 9mm from the tip. The ampoule was foggy. A new design which utilized an alumina tubing to hold only one end of the outside fused silica liner was constructed to solve the problem of the sagging of the liner. During the first run of ZnSe-6, the central zone burned out in the middle of the growth and the run was terminated. Polycrystalline ZnSe about 2cm long with non-planar growth surface and brown-yellow in color was grown. The remaining ZnSe source showed a darker yellowish color than the crystal. The crystal was shaken loose from the ampoule and slid back to the source end and a new growth run was processed. The translation rates for both runs were 3.19mm/day. In the second run, all the material was transported and a single crystal of rather dark yellow color was grown with a slightly convex growth surface at about 3cm from the tip.

Illustration for Simultaneous Measurement of Transport Rate and Partial Pressure

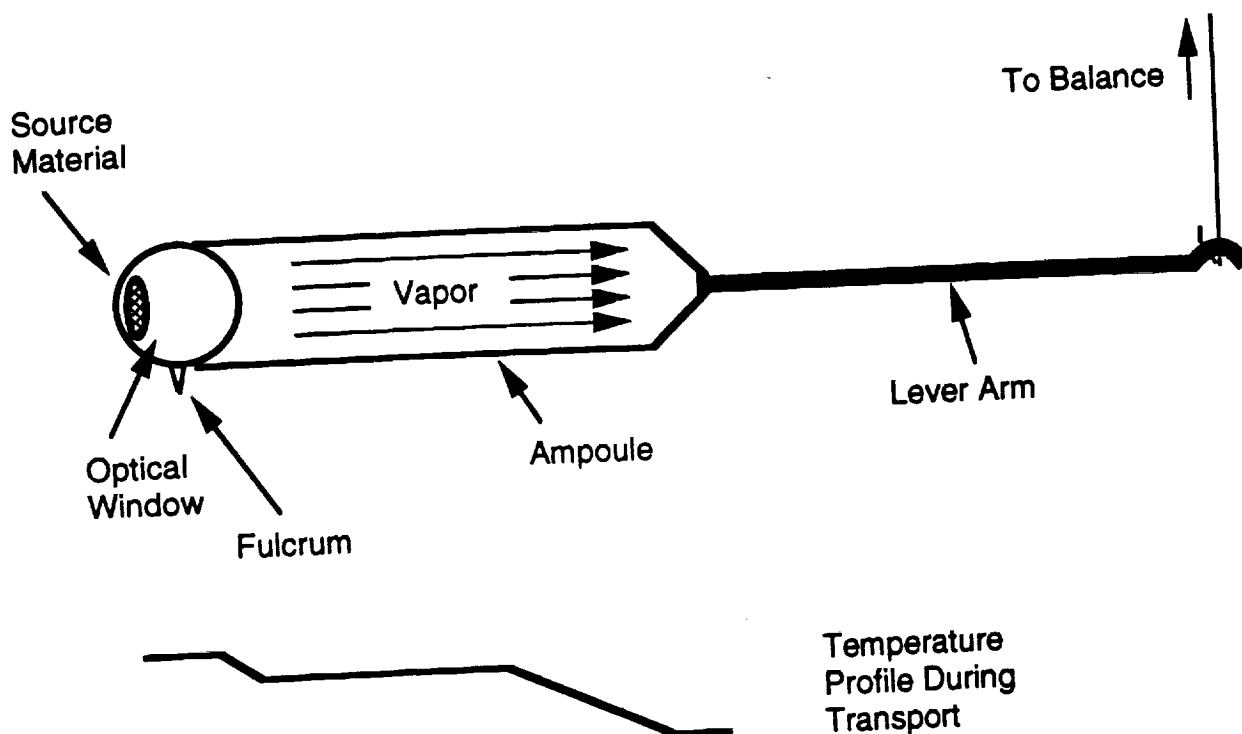


Figure 16

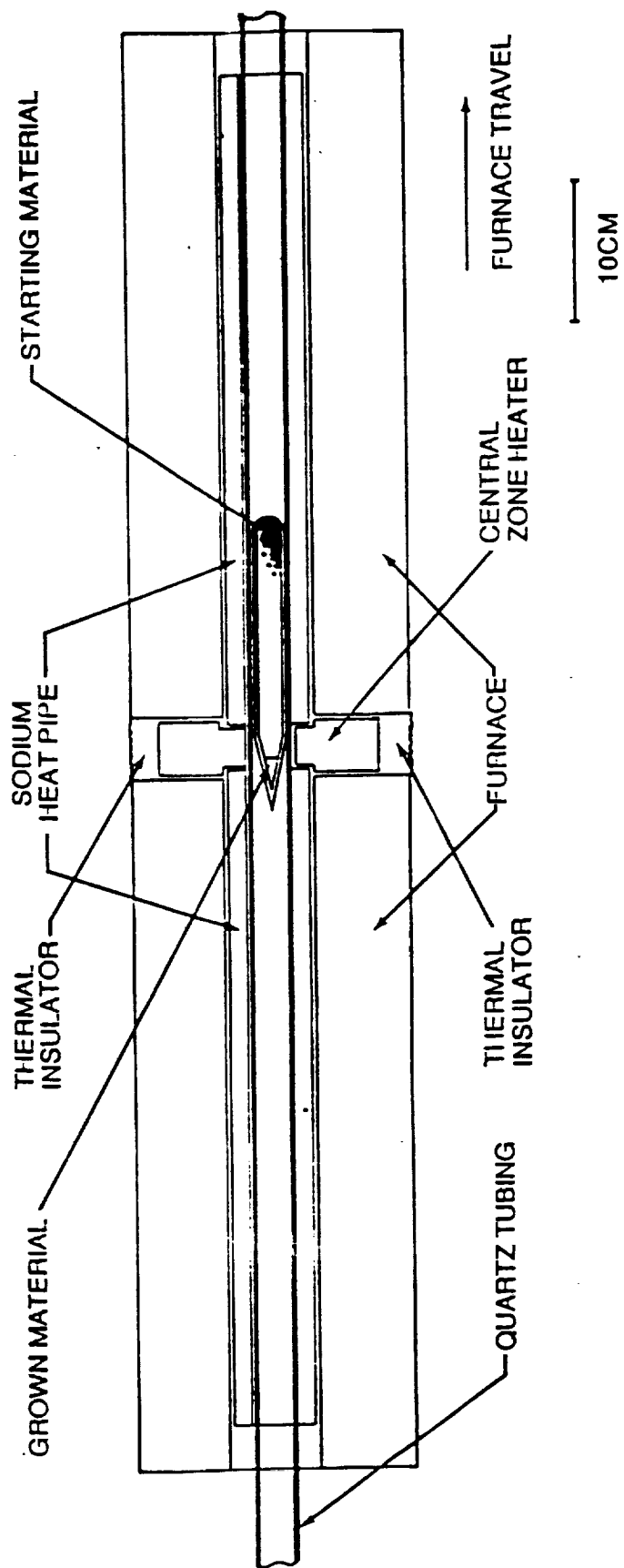


Figure 17

Thermal Profile for ZnSe-5

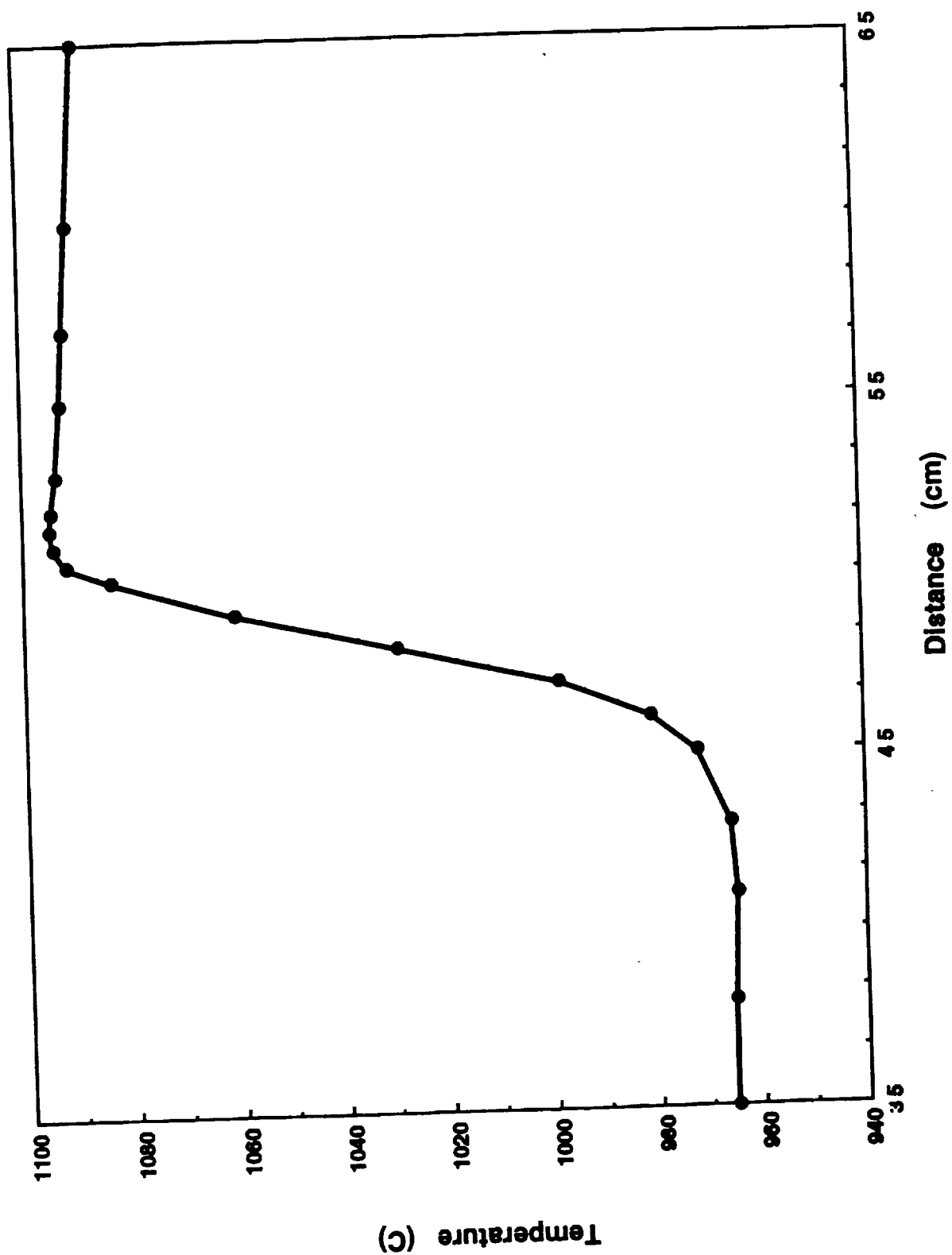


Figure 18

b) work to be performed: The slow growth transport rates were attributed to the two possible contamination sources - the starting materials or the fused silica ampoules. The heat treatment of the source materials will be studied to improve the purity and congruency. The pressure levels of the residual gas desorbed from the ampoules made from various brand name fused silica tubing after long-duration high-temperature annealing will also be investigated. Also, from the results of section 4.3 the transport rate increases an order of magnitude when the growth temperature is increased from 1060 to 1106°C. Another growth furnace which can operate at temperatures higher than 1100°C and provide an isothermal growth temperature without sodium heat pipe (1100°C upper temperature limit) was designed and will be constructed in the next phase to improve the crystal growth rate.

4.6 Characterization

The objectives of the proposed investigation, as stated in Section 2, are to determine the effects of gravity-driven fluid flows on the distribution and density of impurities and defects, stoichiometry, compositional redistribution in the ternary alloys and eventually device performance. To establish the correlation between the growth parameters and the characteristics of the grown crystals we propose to set up a complete and extensive characterization plan. Figure 19 shows the flow chart for the complete analysis of the materials.

a) work performed:

1) X-ray (Laue) diffraction: The facet surface of ZnSe-5 crystal was determined to be (110) planes and the growth direction of ZnSe-6 was [331]. The ZnSe-6 crystal can be cleaved easily as shown in Figure 20. Figure 21 shows the Laue pattern of the cleaved surface and it was determined to be (110) planes.

2) Atomic Force Microscopy (AFM) and Differential Scanning Calorimetry (DSC): Both AFM and DSC were done at Fisk University. The cleaved surface of ZnSe-6 were examined by AFM. Figure 22 shows the atoms on a ZnSe surface and Figure 23 shows a freshly cleaved ZnSe surface with small particles on it. A close-up picture and the depth of profile are given in Figure 24. The size of the precipitate particles is about 50nm which is too small to be detected by the Scanning Electron Microscope (SEM). A SEM picture of the cleaved surface taken in this laboratory is given in Figure 25. To further investigate the nature of the precipitates a ZnSe-6 sample of 53mg was used to make a DSC run. The DSC output is shown in Figure 26 and a clear peak was observed at about 417°C which indicated that pure Zn (melting point 419°C) exists in the sample. However, other characterization techniques, such as Transmission Electron Microscopy (TEM), are needed to confirm that the particles observed in AFM are Zn precipitates.

3) Synchrotron radiation: A slab was cut almost parallel to the growth direction of the ZnSe-6 crystal and was lapped and chemomechanically polished in 2% ethylene glycol solution. The slice was sent to Prof. M. Dudley of State University of New York at Stony Brook for synchrotron radiation analysis. Figure 27 shows the pictures of the slice under optical microscope, reflection and transmission radiation. The slice was thin enough to have transmission image and twin boundaries (TB) can be seen. However, the surface was so rough as to mask the fine features of the transmission image.

b) work to be performed: A part of the ZnSe-6 crystal was sent to Santa Barbara Research Center to study the technique to put on ohmic contact for the Hall measurement and to perform cathodoluminescence measurement. A double-crystal diffractometer was set up in the laboratory and rocking curve diffractometry will be performed. The existing optical transmission and photoluminescence equipment have

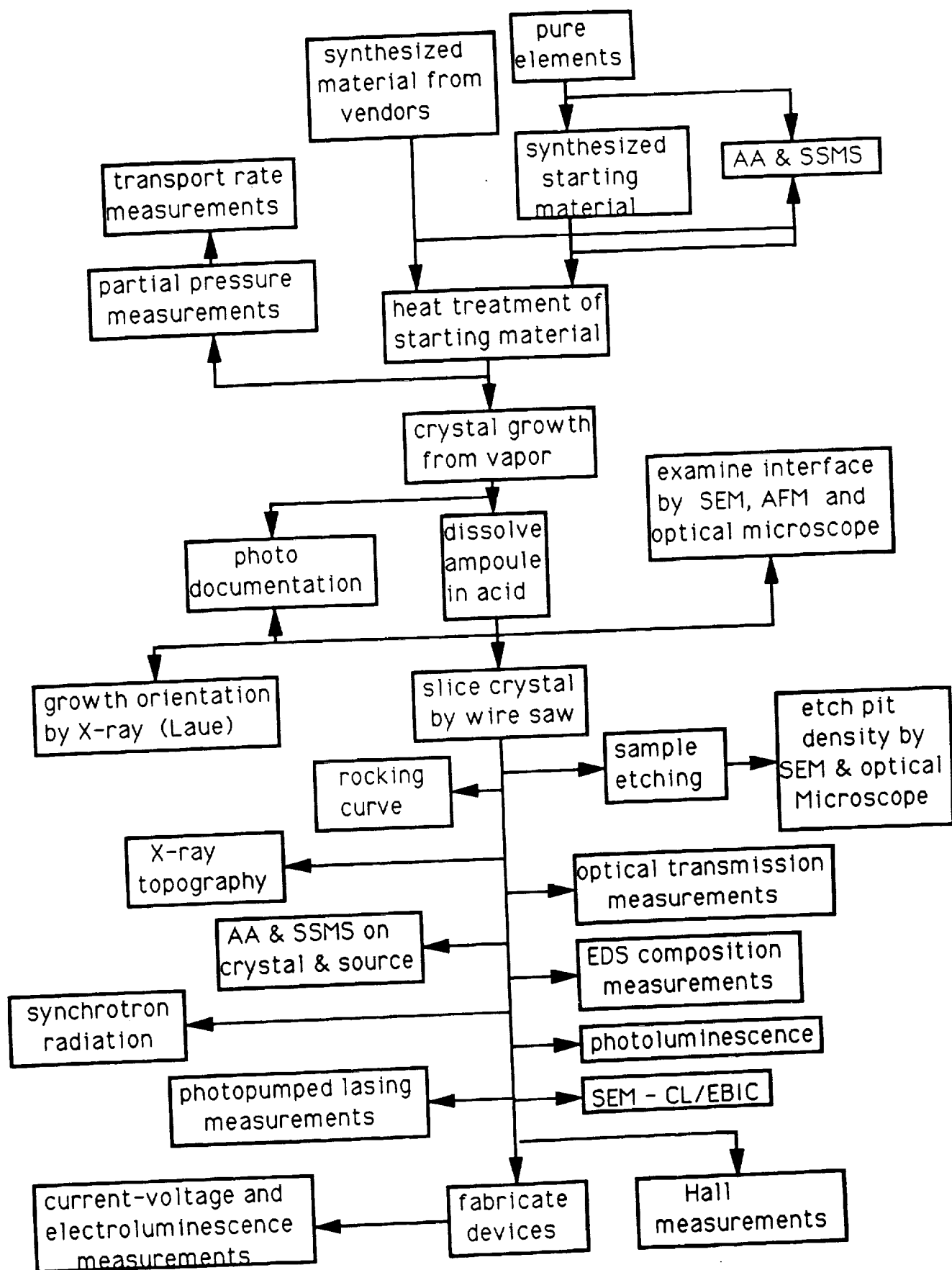


Figure 19 Flow chart of characterization plan

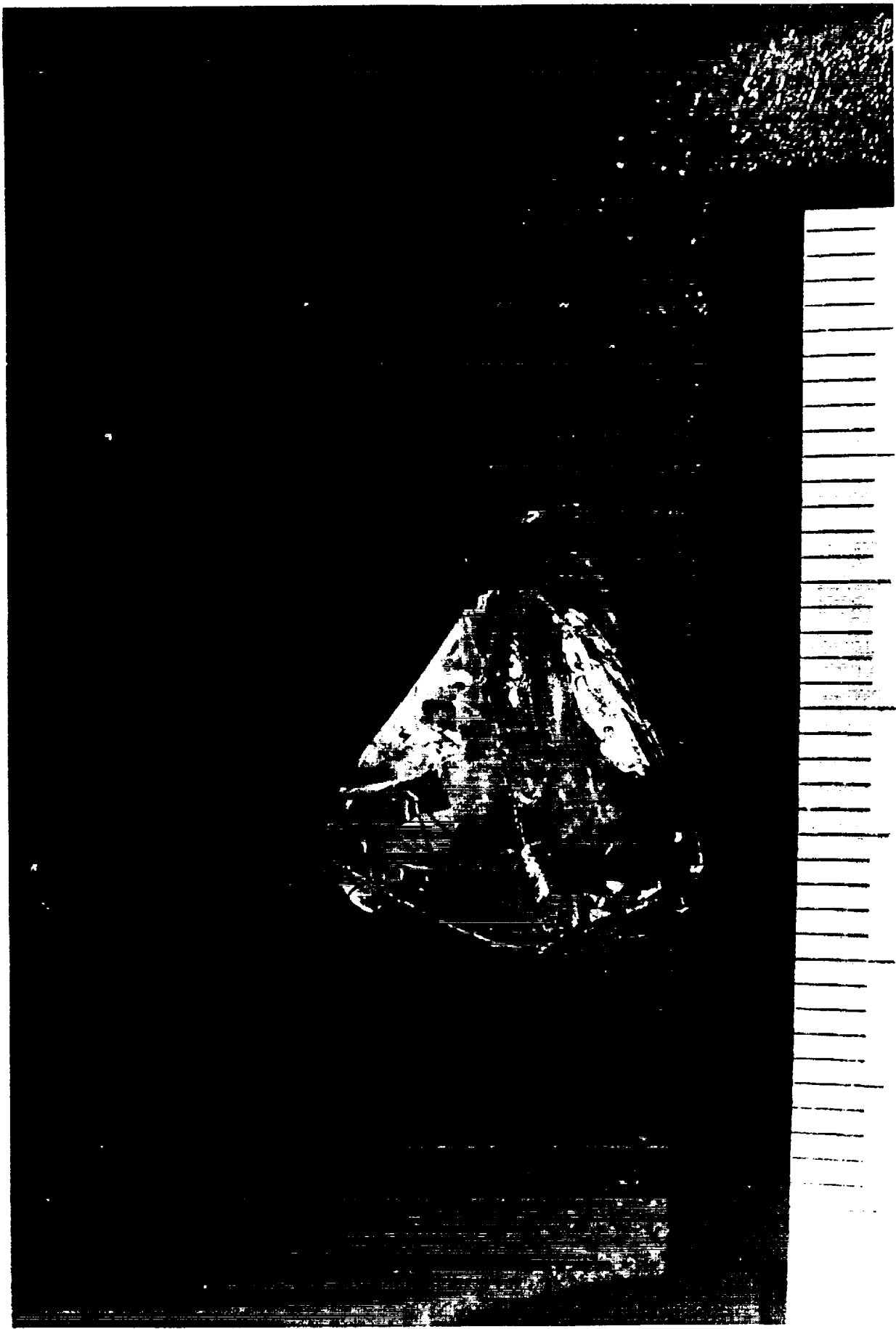


Figure 20

ZnSe-6 Clear.

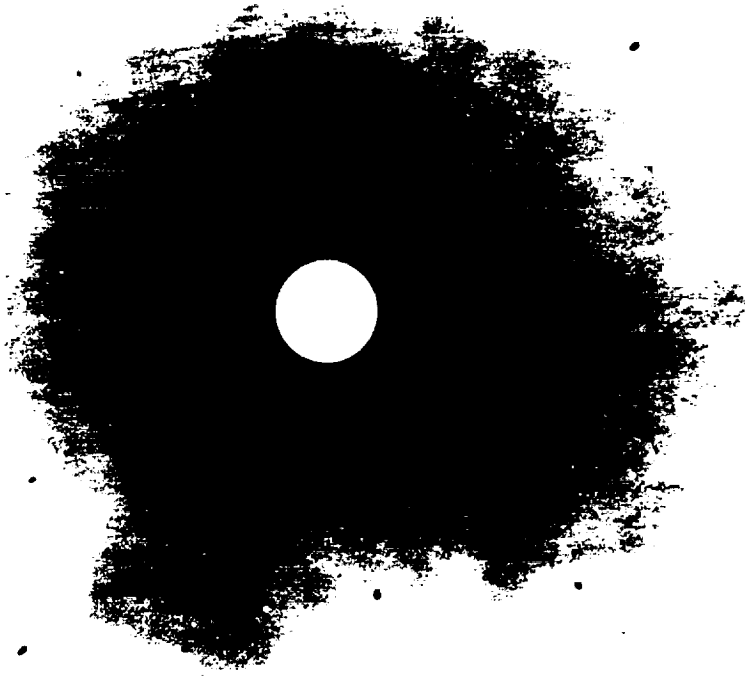


Figure 21

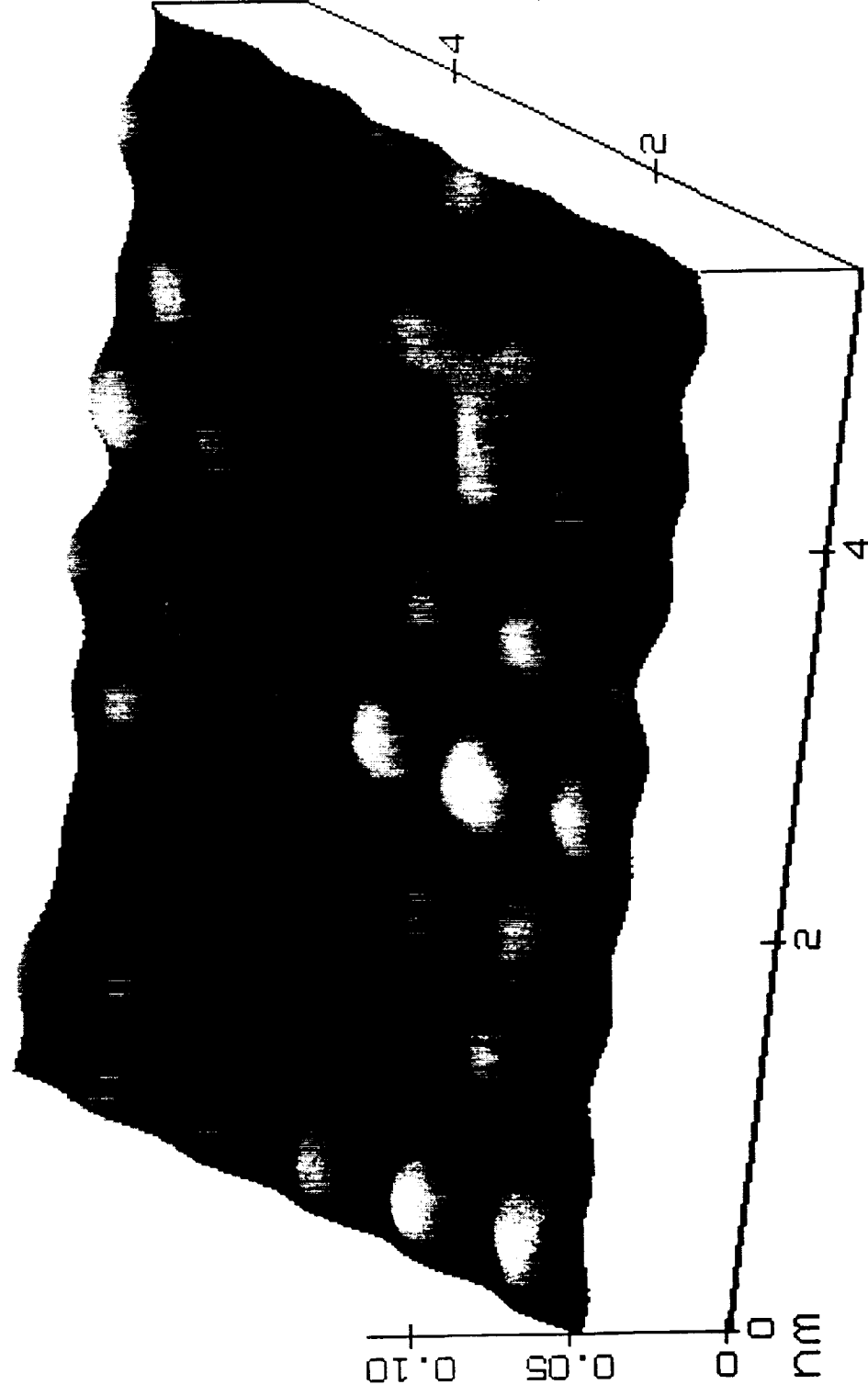
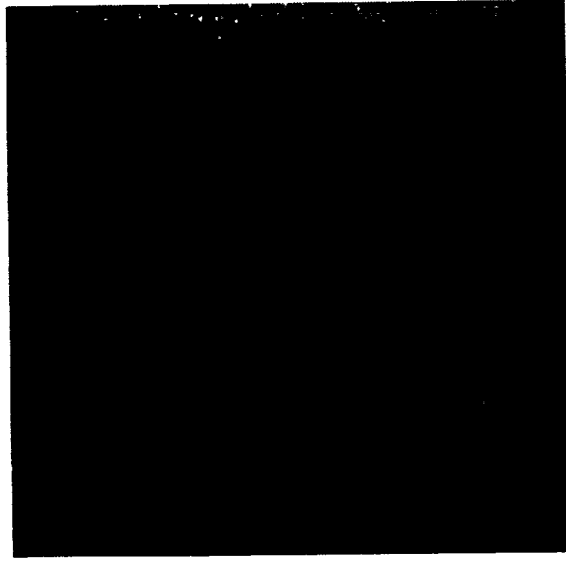
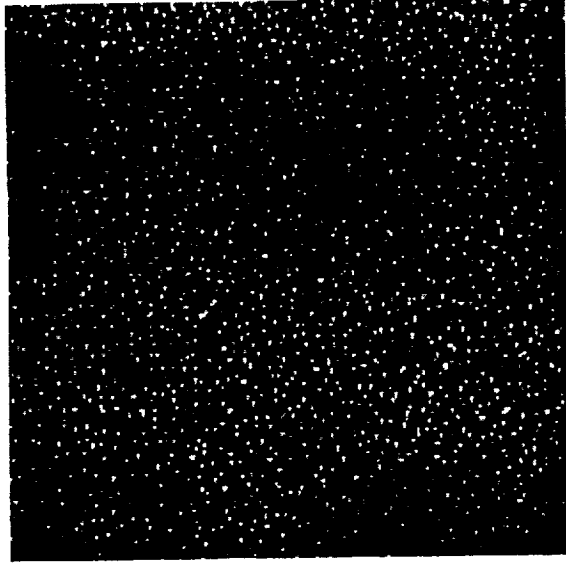


Figure 22 **Atoms on a ZnSe surface**

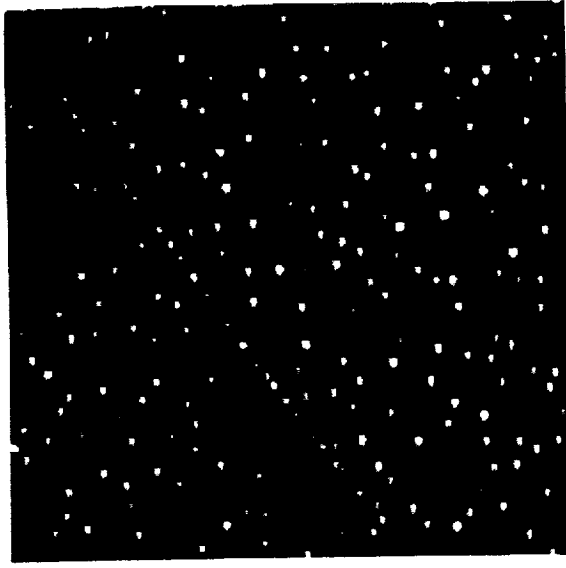
buffer 1 13756.60 nm



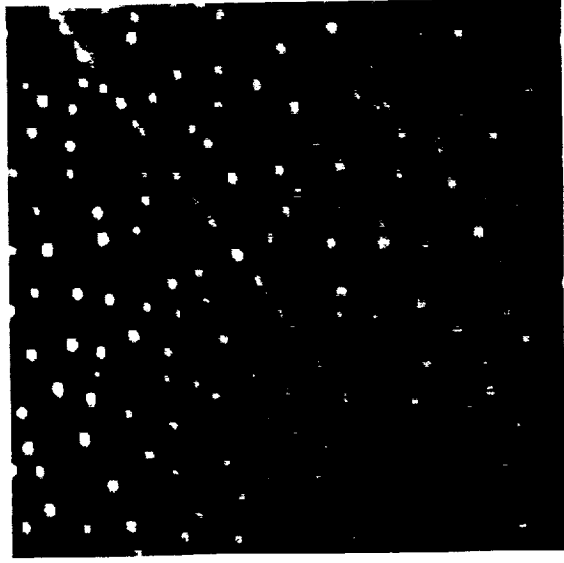
buffer 2 9129.39 nm



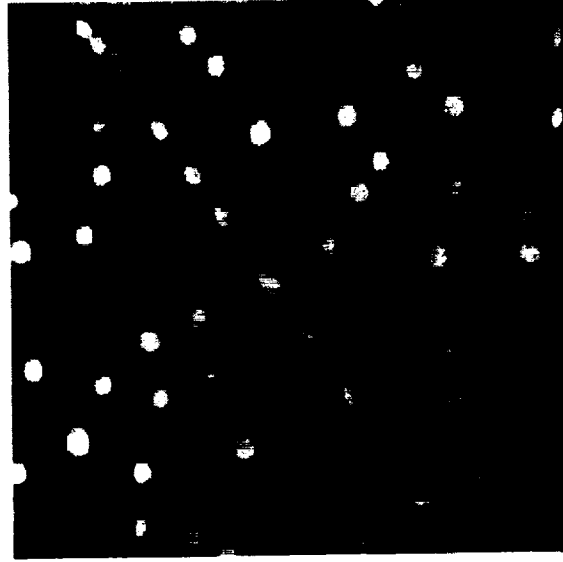
buffer 3 5000.00 nm



buffer 4 3011.43 nm



buffer 5 1558.02 nm



buffer 6 857.43 nm

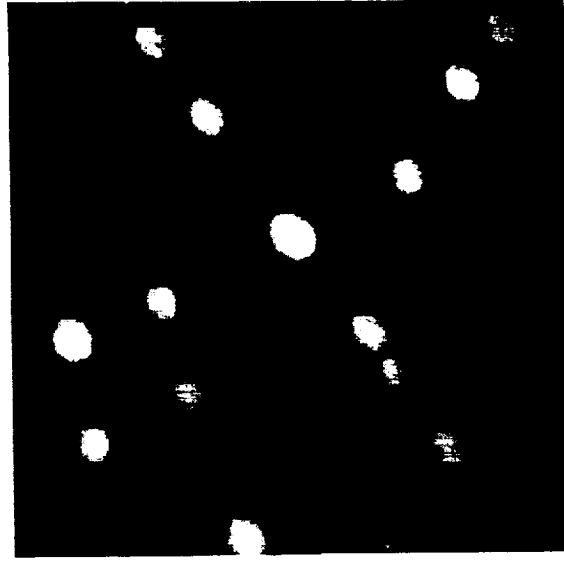


Figure 23 **Freshly cleaved ZnSe showing precipitates**

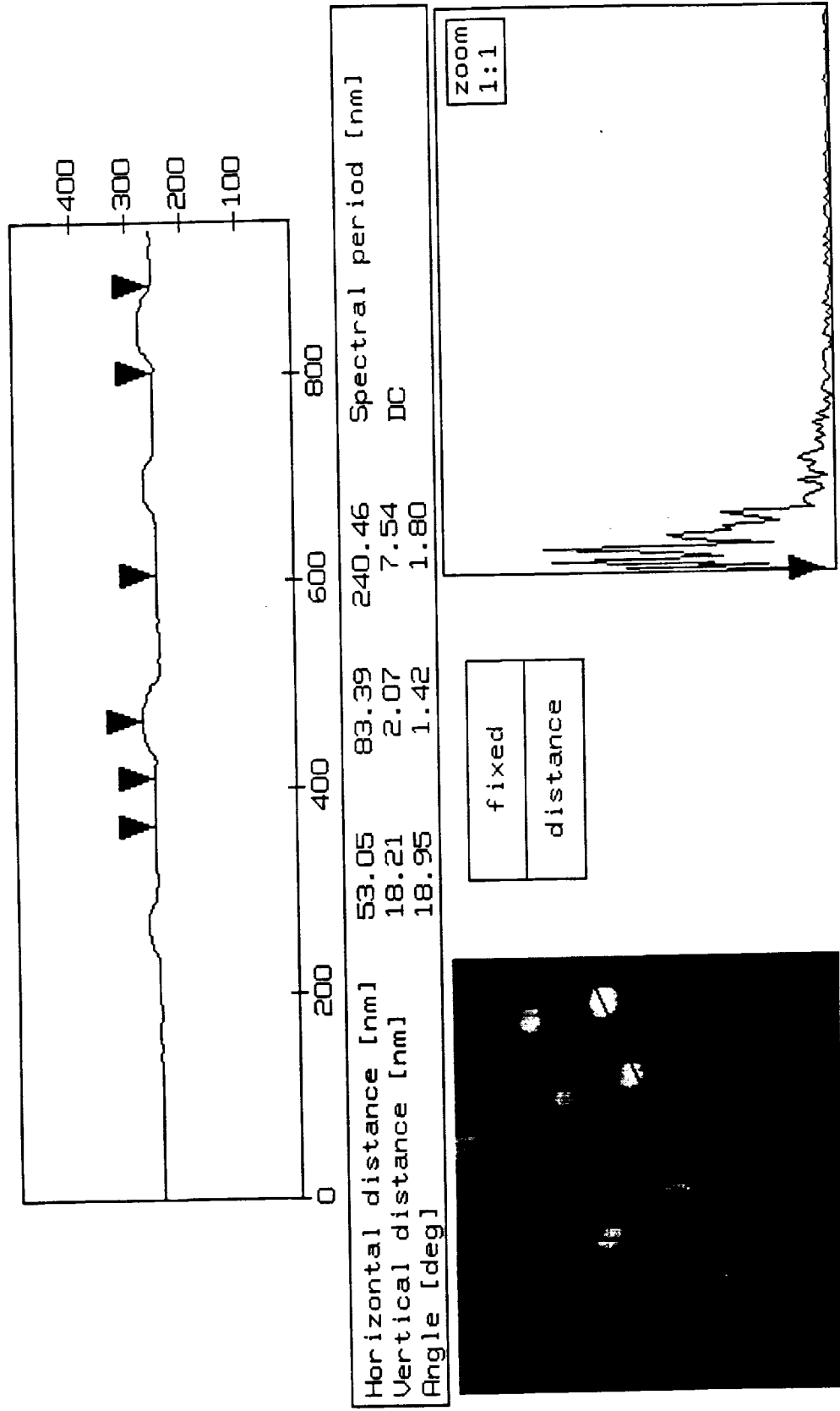


Figure 24

Cleaved ZnSe surface, profile of precipitates

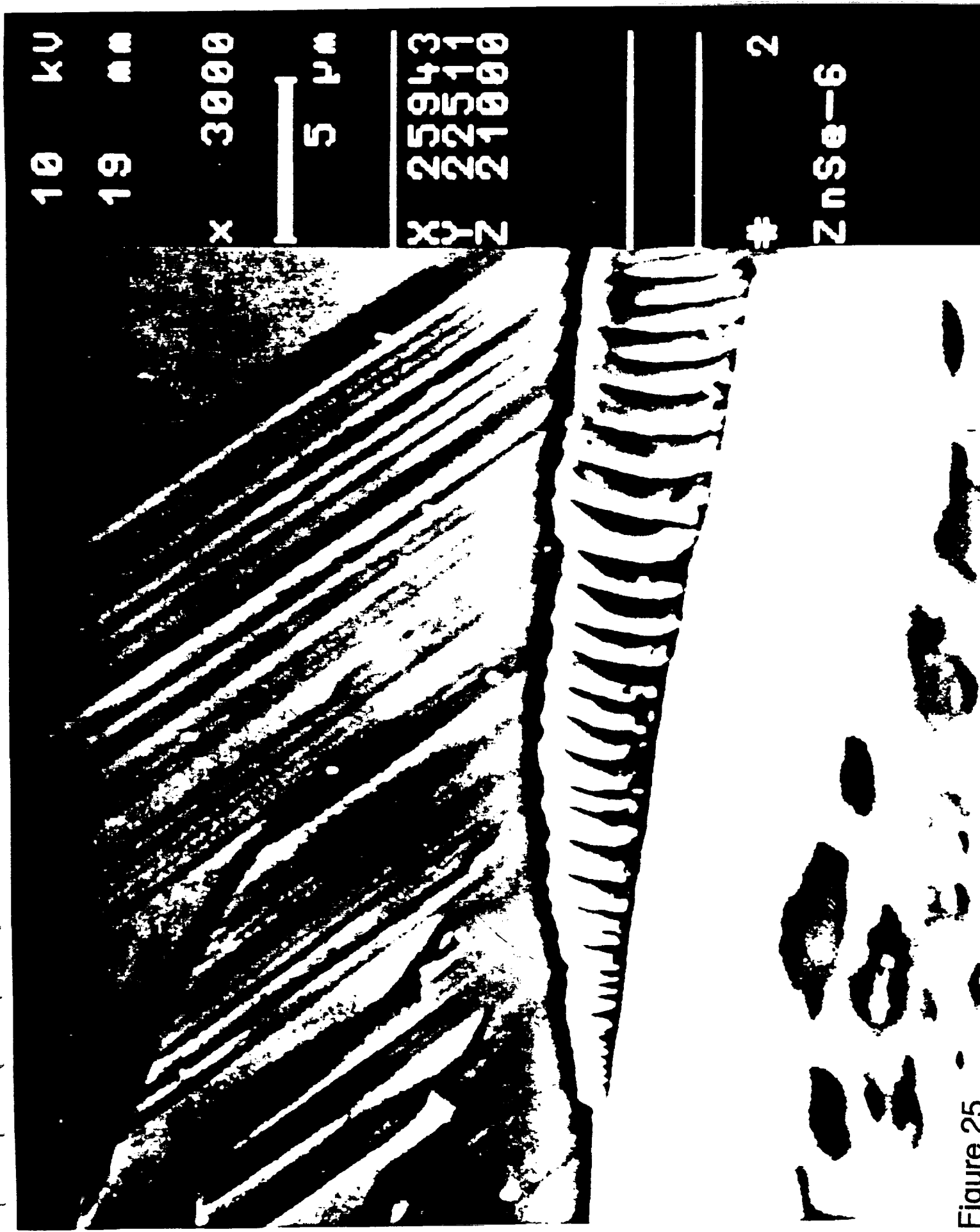
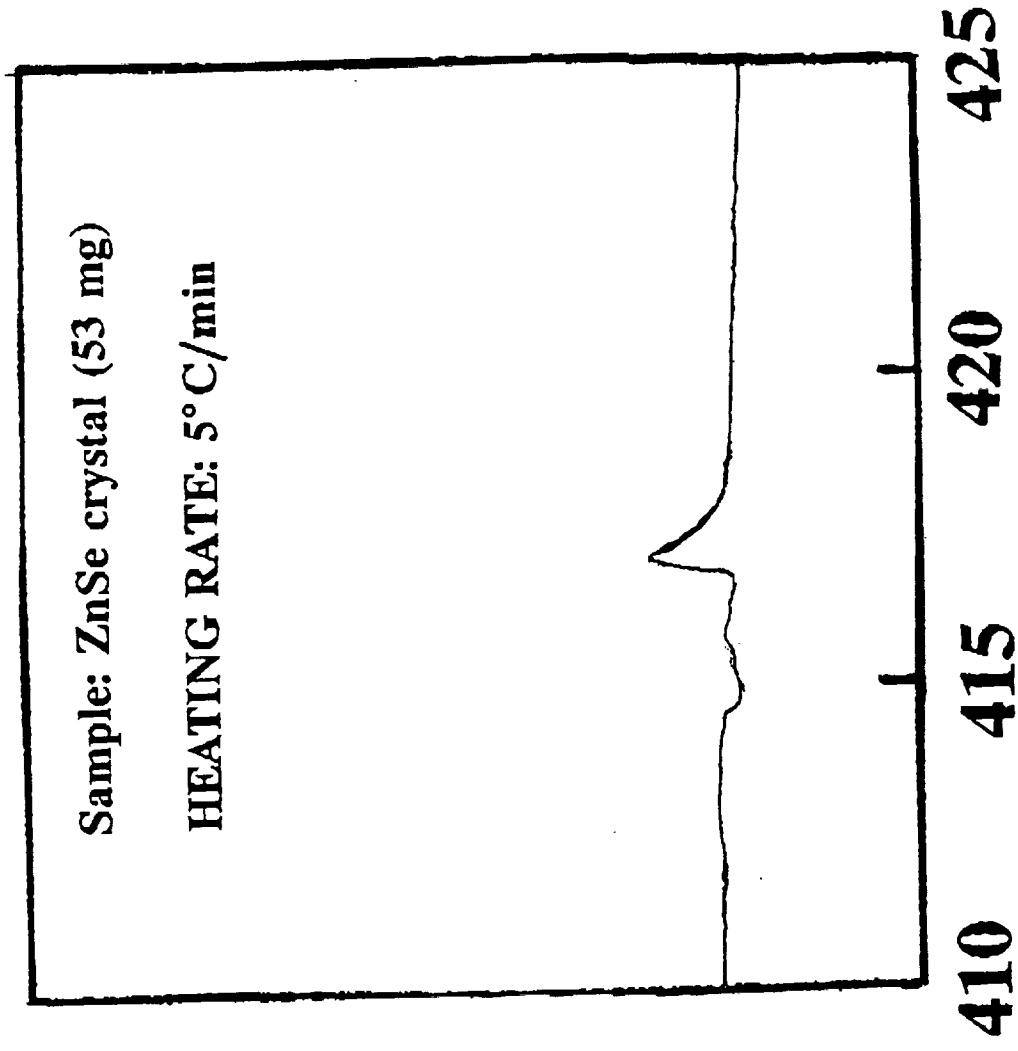


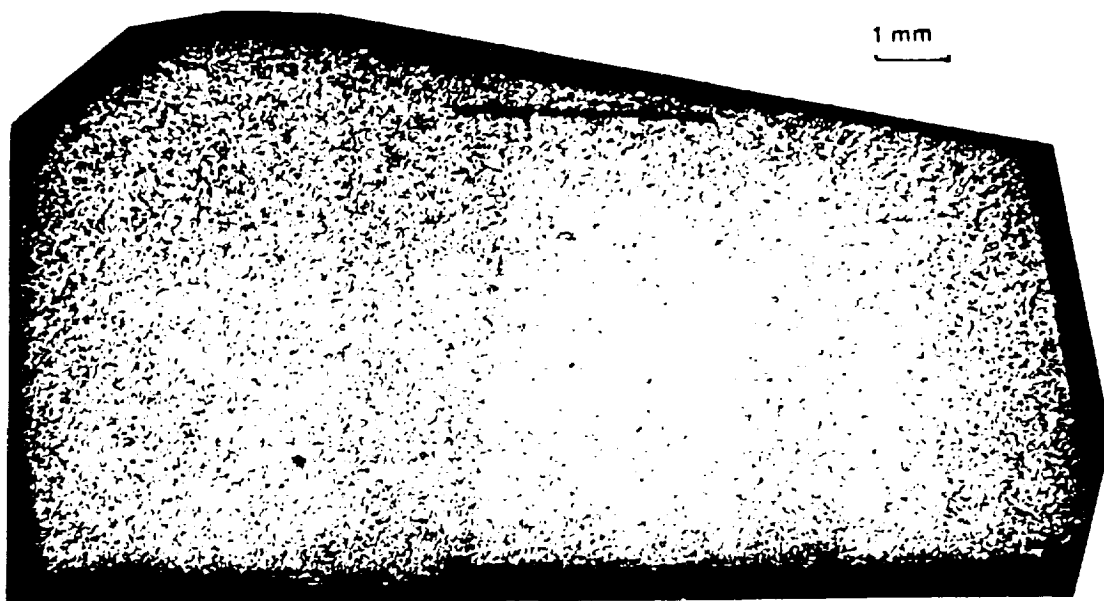
Figure 25

DSC OUTPUT



TEMPERATURE (°C)

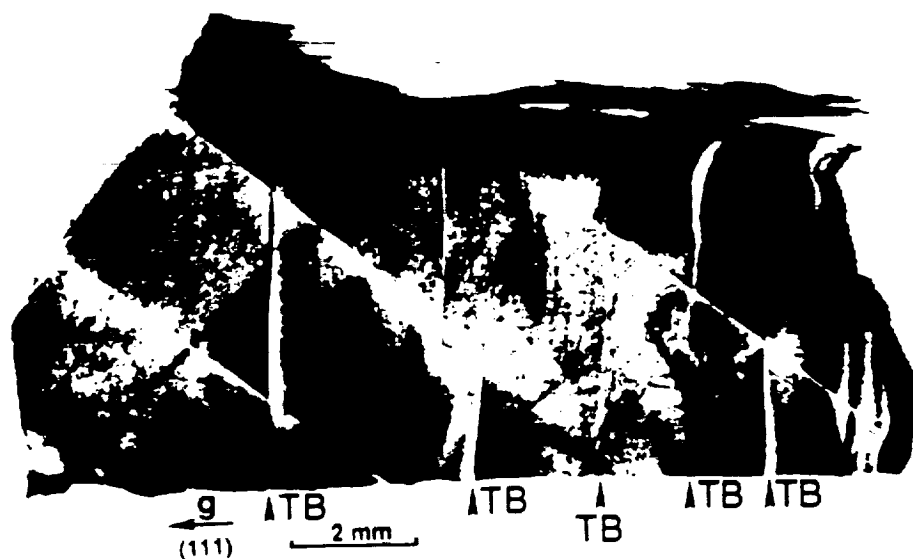
Figure 26



ZnSe - 6 Optical Microscope (after polish and etch in 2% Br Ethylene Glycol)



Reflection Topograph



Transmission Topograph

Figure 27

been modified to have the capability to conduct measurements on ZnSe crystals. Another surface polishing solution, colloidal silica + sodium hypo chloride + water, was recommended by Eagle-Picher Co. Slices will be prepared by this method to have a smoother finished surface for the synchrotron radiation.

5. Discussions

As described above, most of the activities were performed on or ahead of the schedule. The critical issues lie in the aspect of the crystal growth activity. The consistency in the vapor transport rate will be the first issue to be resolved in the next phase of the program. The next critical issue will be to have a well-defined thermal boundary condition to position the initial seed location for the seeded growth. The third issue will be to accurately determine the partial pressure data over the entire ternary compositions so that the transport rates and the compositions of the grown crystals can be evaluated.

References

- [1] for example; M. E. Ozsan and J. Woods, J. Phys. D. 10 (1977) 1335; W. Stutius, Appl. Phys. Lett., 33 (1978) 657; J. Nishizawa, K. Itoh, Y. Okuno and F. Sakurai, J. Appl. Phys. 57 (1985) 2210; X. W. Fan, Z. K. Tang, and H. Tian, J. Crystal Growth 101 (1990) 944; H. Kukimoto, J. Crystal Growth 101 (1990) 953.
- [2] I. M. Catalano, A. Cingolani, M. Ferrara, and M. Lugara, Solid State Commun. 43 (1982) 371; X. H. Yang, I. Hays, W. Shan, J. J. Song, E. Cantwell, and J. Aldridge, Appl. Phys. Lett. 59 (1991) 1681.
- [3] I. Suemune, K. Yamada, H. Masato, Y. Kan and M. Yamanishi, Appl. Phys. Lett. 54 (1989) 981; K. Nakanishi, I. Suemune, H. Masato, Y. Kuroda, and M. Yamanishi, Jap. J. Appl. Phys. 29 (1990) L2420.
- [4] H. Jeon, J. Ding, A. V. Nurmikko, H. Luo, N. Samarth, J. K. Furdyna, W. A. Bonner, and R. E. Nahory, Appl. Phys. Lett., 57 (1990) 2413; J. Ding, H. Jean, A. V. Nurmikko, H. Luo, N. Samarth, and J. K. Furdyna, Appl. Phys. Lett., 57 (1990) 2756; H. Jean, J. Ding, A. V. Nurmikko, H. Luo, N. Samarth, and J. Furdyna, Appl. Phys. Lett. 59 (1991) 1293.
- [5] Y. Kawakami, S. Yamaguchi, Y-H Wu, K. Ichino, S. Fujita, and S. Fujita, Jap. J. Appl. Phys. 30 (1991) L 605.
- [6] V. A. Stadnik, Optics Commun. 68 (1988) 445.
- [7] H. J. Eichler, V. Glaw, A. Kummrow, V. Penschke, and A. Wahi, J. Crystal Growth 101 (1990) 695.
- [8] M. E. Ozsan and J. Woods, Solid State Electron. 18 (1975) 519; J. W. Allen, A. W. Livingstone and K. Turvey, Solid State Electron. 15 (1972) 1363.
- [9] A. Ebina, E. Fukunaga, and T. Takahashi, Phys. Rev. B. 10 (1974) 2495; L. Soonckindt, D. Etienne, J. P. Marchand, and L. Lassabatere, Surface Sci. 86 (1979) 378.
- [10] M. J. S. P. Brasil, M. C. Tamargo, R. E. Nahory, H. L. Gilchrist, and R. J. Martin, Appl. Phys. Lett. 59 (1991) 1206.
- [11] for example; M. M. Faktor and I. Garrett, Growth of Crystals from the Vapour (Chapman and Hall, London, 1974); Ching-Hua Su, J. Crystal Growth 80 (1987) 333.
- [12] J. P. Schwartz, T. Tung, and R. F. Brebrick, J. Electrochem. Soc. 128 (1981) 438.
- [13] K. C. Mills, Thermodynamic Data for Inorganic Sulphides, Selenides, and Tellurides (Butterworths, London, 1974).
- [14] H. Wiedemeier, F. C. Klaessig, E. A. Irene, and S. J. Wey, J. Crystal Growth, 31 (1975) 36; H. Wiedemeier, H. Sadeek, F. C. Klaessig, M. Norek, and R. Santandrea,

- J. Electrochem. Soc., 124 (1977) 1095.
- [15] Ching-Hua Su, S. L. Lehoczky, and F. R. Szofran, J. Crystal Growth 101 (1990) 221.
- [16] Ching-Hua Su, S. L. Lehoczky, and F. R. Szofran, presented at ACCG/East-2 Conference, Atlantic City, New Jersey, Oct. 19-21, 1988.
- [17] Ching-Hua Su, M. P. Volz, D. C. Gillies, F. R. Szofran, S. L. Lehoczky, M. Dudley, G.-D. Yao, and Wenyi Zhou, to be published on J. Crystal Growth.



Report Documentation Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle "Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Physical Vapor Transport"		5. Report Date August 23, 1993	
		6. Performing Organization Code	
7. Author(s) Principal Investigator - Dr. Ching-Hua Su, USRA		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address Universities Space Research Association 4950 Corporate Drive, Suite 100 Huntsville, Alabama 35806 (205) 895-0582		11. Contract or Grant No. NAS8-39718	
		13. Type of Report and Period Covered Final Report, Preliminary Definition Phase	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001 and George C. Marshall Space Flight Center NASA/MSFC, Alabama 35812		14. Sponsoring Agency Code NASA/Marshall Space Flight Center	
		15. Supplementary Notes	
16. Abstract Preliminary definition of all of the necessary materials, labor, services, and facilities necessary to provide science requirement definition, initiate hardware development activities, and provide an updated flight program proposal consistent with the NRA selection letter. The major tasks identified in this SOW are in the general category of science requirements determination, instrument definition, and updated flight program proposal. The Contractor shall define preliminary management, technical and integration requirements for the program, including improved cost/schedule estimates. The Contractor shall identify new technology requirements, define experiment accommodations and operational requirements and negotiate procurement of any long lead items, if required, with the government.			
17. Key Words (Suggested by Author(s))		18. Distribution Statement Limited to attached distribution list only.	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages	22. Price